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**2) MICRO-PARTICLE CLASSIFIER:** For solving problems connected with smoke abatement and air pollution, the new Dietert-Detroit micro-particle size classifier will help. It centrifugally divides fine material into grain size fractions, with a range of 4 to 60 microns with precise particle size limits. It measures numerous products, from pulverized coal to inorganic powders. The machine weighs 140 lb net and has power capacity of 230 volts, 60 cycle. *Harry W. Dietert Co.*

**3) TACHOMETER GENERATOR:** The new Type E tachometer-generator developed by *Weston Electrical Instrument Corp.* is designed for use where there may be explosive atmospheres. Available as an ac or dc generator, it is enclosed in a sturdy cast iron housing. The housing measures approximately 10 1/4 in. overall and 4 1/2 in. diam. The ac generator is of rotating magnet type and suitable for speeds up to 5000 rpm; and the dc generator has speeds up to 2000 rpm in either direction.

**4) SORTING MACHINE:** Model C Cyclograph and the new automatic sorter combination are the latest development in cyclograph testing equipment based on original DuMont patents. Sorting up to 300 pieces per min, operation by unskilled labor, and a wide range of test frequencies (2 to 200 kc) are some of the many advantages. *J. W. Dice Co.*

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ful for parts that must remain nonmagnetic after severe cold working, because permeability is approximately 1.002 after a 50 pct reduction with a field of 200 Oersteds, and about 1.018 after an 80 pct reduction. It comes in all sizes and standard gages to 1 5/8 in. OD and shapes whose equivalent round will not exceed 1 5/8 in. OD. Special rollings requiring at least 2000 lb would be required for larger sizes.

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Journal of Metals  
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The AIME Publishes:  
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*Journal of Metals*

*Journal of Petroleum Technology*

# METALS

VOL. 188, NO. 8

AUGUST, 1950

## COVER

The wax injection room of the International Nickel Co.'s precision casting foundry at Bayonne, N. J. These injection machines force wax at pressures from 400 to 800 psi into split molds, the bottom halves of which are refrigerated to speed was solidification. Tolerances of 0.005 in. per inch of part dimension can be held on precision cast parts. Straightness can be held on long, slender parts, but it is often difficult to hold to extremely close dimensions in two or three planes. Parts are made for jet aircraft, pumps and valves, oil atomizers, scarfing blow pipe heads, and other products requiring extremely accurate parts difficult to form by other methods.

## FEATURES

Journal of Metals REPORTER	967
"Drift of Things"	968
Engineering Employment Service	956
Authors in This Issue	965

## NEWS

Water Resources Policy Deployed	971
Alcoa Anti-Trust Suit Ends	973
Armco Elevators to Speed Furnace Charging	973
Short Cuts	957
AIME Activities	970
Coming Meetings	971
IMD Fall Meetings	971
Personals	974
New Members	972
Manufacturers' News	958

## TECHNICAL ARTICLES

Flow and Velocities of Air and Waste Gases in Open Hearth Furnaces	976
Open Hearth Bath Temperature Measurement and Control	980
Oxygen for Carbon Reduction and Temperature Pickup	982
Ferrochromium from Low Grade Chromite Ores and Concentrates	984

## TRANSACTIONS

Electrical Resistivity of Titanium Slags	James L. Wyatt	989
Intermittent Oxidation of Some Ni-Cr Base Alloys	B. Lustman	995
Austenitic Formation During Tempering, and its Effect on Mechanical Properties	E. F. Bailey, W. J. Harris, Jr.	997
Recrystallization Reaction Kinetics and Texture Studies of a 50 Fe, 50 Ni Alloy	W. E. Seymour, David Harker	1001
Production and Examination of Zn Single Crystals	D. C. Jillson	1005
An Experimental Survey of Deformation and Annealing Processes in Zinz	D. C. Jillson	1009
Discussion—Institute of Metals Division		1019

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For further information on any product or for your copies of the free publications, fill in the coupon below and send it to the *Journal of Metals*.

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**13) WELDING CABLE:** *Lincoln Electric Co.* announces a new welding cable for electrode and ground, Linconductor Cable. Neoprene covered, it passed all tests for 10-year aging by exposure, resistance to flame burning, and copper oxidation. New features permit a low cost cable equal to premium rubber covered cable.

**14) CORE TRUCKING:** Electric industrial trucks for moving heavy loads of hot cores relieve physical exertion for foundry operators and reduce materials handling costs. With a Transporter, the operator can walk in front of the cores and be away from the heat. *General Foundries Co.*

**15) PORTABLE CUTTERS:** *H. K. Porter, Inc.,* presents three new two-hand portable cutters: (1) For extremely hard materials up to  $\frac{3}{8}$  in. diam., (2) for hot steel bars, rods, and wire up to  $\frac{5}{8}$  in. diam. and (3) for expanded metal and heavy gage metal

lathe. These cutters have specially designed center cut jaws with pointed noses to allow cutting in narrow places,  $\frac{3}{16}$  in. capacity.

**16) VARIABLE SPEED MOTOR:** For users of fractional horsepower motors, a new design has been developed by *U. S. Electrical Motors, Inc.* It combines in one unit a Varidrive, which permits instant change of speed in a ratio of 1 to 10, and a heavy duty Syncro-gear for increasing the torque. It is *U. S. Motors'* Type VA-GD and is available in  $\frac{1}{4}$ ,  $\frac{1}{8}$ ,  $\frac{1}{2}$ , and  $\frac{3}{4}$  hp.

**17) ELECTRONIC FLAME CONTROL INSTRUMENT:** Operation of Bessemer converters becomes simple, with high technical accuracy in determining the end point and controlling the carbon, by the use of a new electronic flame control instrument. The operator can determine the silicon, manganese and carbon periods and the unit forewarns the operator of impending manganese boils, reducing loss of metal and time. *Whiting Corp.*





H. V. Flagg



E. H. Reyer



R. T. C. Rasmussen

**H. V. Flagg** (p. 976) is Combustion Engineer for the Armco Steel Corp., Middletown, Ohio, and has been with the company for 23 years. Prior, he worked in byproduct coke plants at Toledo, Cleveland, and Youngstown. He graduated from Pennsylvania State College with an M. S. degree.

**J. A. Creighton** (p. 980) is superintendent of Open Hearths at the Lackawanna Plant of the Bethlehem Steel Co., Buffalo, N. Y. His entire career since 1915 has been in association with this company. He was born in Thomaston, Maine, attended Phillips Andover, and received a degree of B.S. from the Massachusetts Institute of Technology. He is an AIME member and lives at Hamburg, N. Y. His hobbies run to fishing, golf, and bird watching.

**E. H. Reyer** (p. 982), superintendent of open hearths at the Keystone Steel & Wire Co., attended Hedding College, and is an AIME member. He likes fishing, golfing, and hunting.

**R. T. C. Rasmussen** (p. 984) is head of the Ferrous Metals Branch, Metallurgical Div., U. S. Bureau of Mines, at Albany, Ore., specializing in iron, steel, and the ferroalloys. He began as Research Fellow at the Missouri School of Mines and Metallurgy, following which he went to Salt Lake City as Metallurgist for the Bureau. He served in Japan as Scientific Consultant to SCAP. An AIME member, he enjoys the camera and fossil and mineral collecting near his home.

**F. W. Wessel** (p. 984) joined the U. S. Bureau of Mines at Albany, Ore., as Metallurgist in the Northwest Electrodevelopment Laboratory in 1948, after a short term at the Getchell Mine, in Red Howe, Nev. A New Yorker by birth, he attended MIT, New York University, and the University of Nevada. He joined the AIME in 1934.

**James L. Wyatt** (p. 989) has been Development Engineer in the Titanium Div. of the National Lead Co. at South Amboy, N. J., since graduating from the University of Kentucky with B.S. and M.S. degrees in Metallurgical Engineering. He was born in Williamsburg, Ky., and attended Lafayette High School in Lexington. He is an AIME member and around his home in New Brunswick, N. J., enjoys photography and flying. He holds a commercial pilot license.

**Benjamin Lustman** (p. 995) is with the Atomic Power Div. of Westinghouse Electric Corp., at Homestead, Pa. He was born in Pittsburgh and received his D.Sc. from Carnegie Tech. Prior to joining Westinghouse he worked three years for Standard Steel Spring Co., a year in the Metals Research Laboratory of Carnegie Tech, and a year for International Mining & Chemical Corp., at Austin, Texas. He has contributed to AIME Transactions, and wrote the section on *Oxidation* for the 1948 Metals Handbook.

**William J. Harris, Jr.** (p. 997) is with the Ferrous Alloys Branch of the Naval Research Lab at Washington, D. C., planning, directing and supervising research in ferrous physical metallurgy. During World War II he was in charge of Navy research and design of aircraft armor and installation. In 1950 he received the Annual Award of the Institute of Metals Div. Born in South Bend, Ind., he received degrees of B.S., Ch.E. and M.S.E. from Purdue, and from MIT he received a Sc.D.

**D. C. Jillson** (p. 1005), Senior Investigator of the Metal Section, New Jersey Zinc Co., Palmerton, N. J., was born in East Orange, N. J. Swarthmore College and Yale University are his alma maters—a B.S. in 1931 and Ph.D. in 1949. An AIME member, he is director of the Choral and Clambake Society of Lower Towamensing. He also enjoys swimming, tennis, and golf.



\* A mobile steel drum and barrel factory has been designed by a Dutch company to supply temporary needs for drums in remote regions or where demand precedes plant construction. It is fully equipped for production of drums, consisting of some 30 units (trucks, trailers and semi-trailers carrying machinery and a workshop; an electric generating plant; and kitchen, living and sleeping accommodations for the operators).

\* By converting kinetic energy of a small electric motor rotor into potential energy in a spring, which is then used to accelerate the rotor rapidly in the opposite direction, the motor can be reversed in 3 to 4 milliseconds. The rapid reversal motor was developed for electronic computing machines.

\* Front surface mirrors with aluminum reflecting surfaces are recommended for maximum or precise reflectivity, studies made by the Army Engineer Research and Development Laboratories reveal.

\* Nation-wide tests are being made on a new technique in drilling teeth. The method involves an abrasive directed through a small hole in a carbide die, and, on the principle of shot-blasting, drills the tooth. The nozzle can be positioned to drill small crevices, and speed of drilling is increased. Dentists can work right up to the nerve without pain, and there is no rise in temperature caused by friction. The equipment permits, by a turn of the dial, a less abrasive mixture at lower velocities to clean and polish teeth.

\* A hole half the diameter of a human hair, measuring 0.0006 in. diam, has been drilled in metal at the Naval Ordnance Laboratory at White Oak, Md. Made in platinum for the hydraulic system of a new Navy weapon, it is the smallest hole ever drilled in metal in this country. The work was done on a jeweler's lathe, using an ohmeter to indicate drill contact.

\* Oxygen injection is standard practice when extra openhearth production is needed at Keystone Steel & Wire Co. Production of 14 to 15 tons per hr is obtained from a furnace more than 250 heats old, such a furnace formerly producing about 11.5 tons per hr at this age. One furnace was producing more than 14 tons per hr at the time of shutdown at 411 heats.

\* Pyrometric control experience in openhearth practice has resulted in reduced tapping temperatures, increased mold life, increased stool life, improved pouring practice, and improved steel quality. The pyrometer used is a platinum: platinum-rhodium thermocouple type with a high speed electronic recorder. The aim is a minimum tapping temperature that will give a heat, free from skull.

\* The Sorel smelter, which will reduce Allard Lake titanium ores, will utilize five six-electrode rectangular electric furnaces. Furnace hearth size will be about 18 x 50 ft, and the furnace will smelt about 300 tons of ore per day, producing 100 tons of iron and 130 tons of 70 pct  $TiO_2$  slag. The furnaces will be fed continuously by gravity from charge bins, and tap at intervals of 4 hr or more. Slag will be transferred to a high speed casting machine, using cast iron molds, then crushed for shipment to pigment producers. The iron will be treated to reduce its sulphur content to 0.03 to 0.05 pct, and then cast into small pigs or ingots for shipment to steel mills.



# Drift of Things . . . . . as followed by *Edward H. Robie*

**M**OST students of the Russian situation seem to think that the Korean war will not extend beyond that country. If that proves true, the mineral industry need not anticipate more than a temporary fillip in the demand for its products. None of the controls and allocations of World War II seem likely. Considerably more power than yet has been exerted will be necessary to push the North Korean aggressors back into their own country, but the consumption of war matériel should not be large. However, the same type of outbreak may be expected from time to time in several other Communist-dominated countries so United Nations forces must be more ready than they were in Korea to oppose force with force. This will mean that a larger proportion of the world's mineral output would be utilized for munitions, even though not immediately consumed.

The present situation indicates the need for a better organized United Nations police force. Some plan should be ready for execution whereby forces from member countries can be immediately despatched to areas where trouble threatens or military force must be opposed. The United States cannot and should not police the world. The war in Korea had to be assumed for the present by the United States alone, even though it was voted by the United Nations; but it would further the conception of the United Nations idea if no nation, and especially the United States, completely dominated such an effort.

Also, the veto power in the United Nations in such cases as this should be removed. Though Soviet Russia has been blamed for using it to excess, the United States, when the United Nations was organized, was one of those that insisted on this provision in the charter. It was only luck that the Soviet representatives, pouting about the nonrepresentation of Communist China, were absent when the Security Council voted that North Korea, as an aggressor, should be opposed. Had they been present the vote of censure would have been vetoed. No nation should have the power to veto action just because its own interests are concerned. This is just the time when world opinion should govern.

Proponents of world government have long advocated codification of international law. Such law is badly needed in the present instance. It would certainly define what is meant by "aggression". By the Russian definition, the South Koreans or the Americans—it is not entirely clear which—were the aggressors in Korea, cruelly attacking the peaceful inhabitants of North Korea. If this was true it was indeed fortunate that North Korea had immediately available an overwhelming military force that could overrun the aggressor's country as soon as they had fired the first shot across the border.

## Will You Help?

All organizations like to grow. It is an indication of health and good management. Growth normally results in greater economy of operation, increased welfare of the staff, greater profits to the stockholders, and better and cheaper products for the customers. These factors apply equally to a company owned by stockholders or to a co-operative enterprise like the AIME. With the AIME, however, the members are the stockholders and get the profits, tangible or intangible, achieved by growth. The members are also, to a large extent, the customers, getting the benefit of lower unit costs on larger production.

Though the Institute has had remarkable growth—

from 7868 members at the beginning of 1934 to 16,344 at present—the membership could easily be 20,000. A more powerful organization, with greater prestige, would result. Meeting attendance would increase, and thus the opportunity for more professional contacts. The financial benefits would be equally great. If 4000 new members were added to the rolls in the next year, and 3000 of them were Associate Members and Members, there would be an increased income of \$60,000 in initiation fees and a like amount in dues. If the other 1000 were Junior Members without initiation fees, another \$12,000 would be added, or \$132,000 in all. The expense of servicing these additional 4000 members would be nothing like \$132,000. The difference would mean increased services and privileges, at a lower cost to members.

In the last month every member has been asked by mail to suggest the names of good prospects. It is hoped that this request will be productive of a large number of names, of which a good proportion will eventually be found in the Directory. Still more appreciated will be the successful effort of a member to obtain a formal application for membership. If you do not have a blank, just ask us for one when you send in the card.

There is no better way in which AIME members can feather their own professional nest. So send in that card—or a filled out application—now, if you have not already done so.

## Manganese and Chrome

We are getting no more manganese and chrome ore from Russia. She first served notice late in 1948 that manganese ore shipments would be restricted, and there was much more or less hush-hush palaver in Government and steel circles as to what could be done about it. Manganese is an absolute necessity in almost every kind of steelmaking process, nullifying the effect of oxygen and sulphur. From ½ to ¾ lb is used per ton of steel, and with the steel industry operating at over 100 pct of capacity, a good supply of manganese is vital.

Russia, our No. 1 source, supplied 427,000 tons of manganese ore in 1948, and 81,000 tons in 1949, making token shipments on existing contracts that have now expired. The deficiency fortunately has been made up by increased shipments from the Gold Coast and the Transvaal in Africa, and from India and Brazil. The Nsuta mine, in the Gold Coast, is the largest single source of manganese in the world. These sources made up for the deficiency in Soviet shipments last year. Plenty of manganese exists at various places in the United States, but it is too low grade to be commercial. Nevertheless, the deposits have been and are being investigated and concentration methods developed to meet a possible emergency. Also, the 10 pct manganese content of steel-furnace slags offers a possible source.

Chrome ore, like manganese, has to be imported, and to substantially the same amount. Lacking the Russian supply, more will have to be obtained from our other principal suppliers—the Union of South Africa, Cuba, Southern Rhodesia, and the Philippines. Chrome is needed for the refractory and chemical industries as well as for steel.

Russia's cessation of exports was in retaliation for the ban the United States put on shipment of machinery or capital equipment that might be used for war preparations. This includes practically everything. Their principal export to us now is furs.





## Dr. C. H. Mathewson Retires From Yale: Mathewson Medal Established

At a testimonial dinner for Dr. C. H. Mathewson on the eve of his retirement from the faculty of Yale University, D. H. McLaughlin, president of AIME, announced the institution of the Mathewson Medal and Certificate. The award will be made for the paper or series of closely related papers with at least one common author which represents the most notable contribution to metallurgical science. The paper must have been presented at one of the meetings of the Institute of Metals Div., of AIME, and have been published in the Institute Transactions. This award will replace the existing Institute of Metals Div. award.

The testimonial dinner was held June 23, with about 150 in attendance. S. W. Dudley, a Dean Emeritus of the Yale Engineering School, delivered the testimonial. Mr. Mathewson, after graduation from Sheffield Scientific School, Yale University, in 1902, started teaching as an Assistant in Chemistry at Massachusetts Institute of Technology, and in 1904 was appointed Austin Fellow of the Institute, spending two years under Prof. Tammann at Göttingen.

He returned in 1906 to MIT, and in 1907 became a member of the Sheffield Scientific School and the Yale School of Engineering faculty. During his service at Yale he was instructor, assistant professor, and since 1919 he has been professor and chairman of the Dept. of Metallurgy. Dr. Mathewson's fields of research included: 1 Phase relationships in alloy systems; 2 The mechanical properties of metals and alloys, principally in relation to constitution and thermal treatment; and 3 The mechanisms operative in plastic deformation and strain hardening.

Dr. Mathewson was IMD lecturer in 1928, presenting a pioneer paper on "Twinning in Metals." In 1932 he received the James Douglas Gold Medal of AIME; in 1943 he was president of AIME; and in the same year was the Edward DeMille Campbell lecturer before the American Society for Metals. In 1947 ASM awarded him its Gold Medal. For meritorious service to Yale University, he was selected for the Yale Engineering Assn. Award of Merit for 1950.



## F. H. Brownell Receives Rand Medal

Francis H. Brownell was awarded the Rand Medal at a dinner following the AIME Board of Directors meeting on June 22. Awarded from time to time for distinguished achievement in mining administration, the Medal was scheduled for presentation to Mr. Brownell at the Annual Banquet. The presentation was postponed because of Mr. Brownell's enforced absence from the city.

President D. H. McLaughlin presented the Medal, the citation of which read: "For sound leadership in the administration of nonferrous mining and metallurgical enterprises and for outstanding contributions to society in financial and legal matters relating to the nonferrous metal industry."

Mr. Brownell, now retired, had been chairman of the board of the American Smelting and Refining Co.

## Are You an Associate Member?

Many AIME members holding responsible professional positions are classed as Associate Members rather than Members. This usually is because when they applied for membership their qualifications were not such that they could be elected Members. To qualify for the latter category, an applicant *must have had at least six years' employment in the practice of mineral engineering, or in the application of the sciences to any of the branches of the mineral industry, during at least three years of which he must have held positions of responsibility.*

Associate Members are urged to apply for a change of status to Member as soon as they feel qualified. The prestige of being a Member well justifies the change. No cost is involved, and all fees and privileges are the same. Merely notify AIME headquarters that you wish to apply for the change in status and an application blank will be sent you. Or if you have one of the regular application blanks for membership, merely fill it out and mark it change in status.



## Water Resources Policy Deplored

A committee of the Engineers Joint Council submitted a report to President Truman and his Water Resources Policy Commission that spoke out bluntly against "excessive and unsound" water resources practices. These practices were attributed to competing federal agencies and Congressional "response to pressure and trading," and the committee called for a halt in further authorizations until a uniform policy has been adopted.

The report deplored "ambiguous, uncoordinated and conflicting" Federal policies covering power, irrigation, flood control, navigation and other water resources projects. Although the report did not direct itself to the activities of any particular agency, it cited the fact that the Dept. of the Interior, Corps of Engineers, Dept. of Agriculture, Federal Power Commission, U. S. Public Health Service, Weather Bureau, Coast and Geodetic Survey "and many others" are concerned with one phase or another of water development.

The engineers offered specific recommendations for correcting the existing practices including methods of procedure, authorization, and economics. Copies of the report may be obtained from the AIME without charge as long as the limited supply lasts. If indicated on the request, in the event that the free supply be exhausted, the requests will be forwarded to Engineers Joint Council, which will supply copies for \$1.50.

## AIME Journals Available on Microfilm

An agreement between the American Institute of Mining and Metallurgical Engineers and University Microfilms, Ann Arbor, Mich., will make available to libraries issues of *Journal of Petroleum Technology*, *JOURNAL OF METALS*, and *Mining Engineering* for 1950 in microfilm form.

Microfilm makes it possible to produce and distribute copies of periodical literature on the basis of the entire volume in a single roll, in editions of 30 or more, at a cost approximately equal to the cost of binding the same material in a convenient library binding.

Under the plan, the library keeps the printed issues unbound for circulation from two to three years. When the paper copies begin to wear out or are not called for frequently, they are disposed of and the microfilm is substituted.

Sales are restricted to those subscribing to the paper edition, and the film copy is only distributed at the end of the volume year.

The microfilm is in the form of positive microfilm, and is furnished on metal reels, suitably labeled. Inquiries concerning purchase should be directed to University Microfilms, 313 N. First St., Ann Arbor, Mich.

## IMD Meets With Metal Show

Registration, technical sessions and the annual fall dinner of the Institute of Metals Div., AIME, will be at the Sheraton Hotel, Chicago, Oct. 23 to 25, 1950, during the National Metal Congress and Exposition. Two simultaneous technical sessions have been scheduled tentatively for Monday morning and afternoon, Oct. 23; Tuesday morning and afternoon, Oct. 24; and Wednesday afternoon, Oct. 25. An informal technical session is scheduled for Monday evening, and the cocktail party and dinner will be held Tuesday evening. Registration, which includes a set of reprints of papers, will be \$2.00 for members and \$4.00 for non-members.

Application blanks for hotel reservations have been sent to IMD members, and are available from AIME on request. All applications for hotel space should be mailed either to the Sheraton Hotel or the Chicago Convention Bureau.



## —Proposed for Membership—Metals Branch AIME—

Total AIME membership on Mar. 31, 1950, was 16,397; in addition 4037 Student Associates were enrolled.

### ADMISSIONS COMMITTEE

*E. C. Meagher, Chairman; Albert J. Phillips, Vice-Chairman; George B. Corless, H. P. Croft, Lloyd C. Gibson, Ivan A. Given, F. W. Hanson, T. D. Jones, P. Malozemoff, Richard D. Mollison, and John Sherman.*

*Institute members are urged to review this list as soon as the issue is received and immediately to wire the Secretary's office, night message collect, if objection is offered to the admission of any applicant. Details of the objection should follow by mail. The Institute desires to extend its privileges to every person to whom it can be of service but does not desire to admit persons unless they are qualified.*

*In the following list C/S means change of status; R, reinstatement; M, Member; J, Junior Member; AM, Associate Member; S, Student Associate.*

#### Alabama

*Birmingham—Madden, Robert Houston, Jr. (M).*

#### Arizona

*Hayden—Cullom, John T. (C/S—S-J).*

#### Colorado

*Denver—Goddard, Paul Lacey (A).  
Rangely—Thornton, James T. (R—C/S—S-J).*

#### Illinois

*Chicago—Satek, Frank J. (M).*

#### Kentucky

*Louisville—Ritchey, Neil F. (J).*

#### Michigan

*Dearborn—Ham, John Lowell (C/S—A-M). Hegmann, William George, Jr. (M).  
Detroit—Kasper, Arthur Stanley (J). Printz, Leon Joseph (M).*

#### Minnesota

*Duluth—Purbaugh, C. A. (M).*

#### Nevada

*Reno—Johnson, Walter Burton (C/S—S-J).*

#### New York

*New York—Hausner, Henry Herman (M). Margolin, Harold (C/S—S-J). Stocklager, Edwin Stevens (M).*

#### New Jersey

*Madison—Koebel, Frank E. (A)*

#### Ohio

*Cleveland—Fischer, Hans F. (M).*

#### Oklahoma

*Blackwell—Rowland, Harvey Leon (J).*

#### Pennsylvania

*Jeannette—Carlson, Charles L. (C/S—S-J).  
Philadelphia—Pollock, Daniel David (C/S—S-M).  
Pittsburgh—Loftus, Fred H. (M).  
St. Marys—Honeyman, Robert Newton (C/S—S-J).*

#### Texas

*Houston—Juergens, Raymond John, Jr. (J).*

#### Virginia

*Richmond—Clarke, William Harvey (J).*

#### Brazil

*S. Paulo—Lozano, Eduardo Pyles (C/S—A-M).*

#### Peru

*La Oroya—Mortimer, John Mongrieff (M).*

#### Sweden

*Lulea—Hjerdin, Sven (M).*



## Armco Open Hearth Elevators To Speed Furnace Charging 57 Pct

The elevator system for feeding scrap and other charge materials into the new open hearth furnaces of the Armco Steel Corp., Middletown, Ohio, will be built by the Westinghouse Electric Corp. The installation was described in JOURNAL OF METALS, May, 1950, p. 744. It will speed up the charging operation some 57 pct.

The Westinghouse Elevator Div., designer of the system, has been awarded a contract for the installation of four special hydraulic-type elevators which will serve three furnaces at Armco's new open hearth plant. The elevators will reduce the time needed to charge a furnace from  $3\frac{1}{2}$  to  $1\frac{1}{2}$  hr.

Each elevator will be fitted with a 10 x 20 ft platform which will carry the charge buggies with their loads of scrap and other materials from the yard level up 20 ft to the charging doors of the furnace. The elevators will be designed to lift a 45,000 lb load in 30 secs, with a maximum rating of 60,000 lb. in 38 sec. They will be loaded at right angles to the furnace, and will revolve 90° to permit the charge buggies to be unloaded in line with the furnace doors. The buggies will run on tracks installed on the elevator platforms.

Installation of the elevators, to begin soon, will be completed by Nov. 1. The McGraw Construction Co. is the general contractor for the new open hearth plant.

## Case Teams With Arts Schools

A new curriculum for combined liberal arts and engineering education has been announced by six middle western colleges. The plan, designated the "Binary Curriculum," involves three years study at one of the liberal arts colleges, and two years and a summer of work at the engineering school, Case Institute of Technology, Cleveland.

Upon completion of requirements at each institution, the student will receive a BA degree from the liberal arts college and a BS in a specialized engineering field from Case. Liberal arts schools participating include Coe College, Cedar Rapids, Iowa; DePauw University, Greencastle, Ind.; Marietta College, Marietta, Ohio; Oberlin College, Oberlin, Ohio; and Ohio Wesleyan University, Delaware, Ohio.

The student must be first accepted by one of the participating liberal arts schools and complete the liberal arts course. He may then be recommended by the college for admission to Case to continue the program there. Under the plan, students will receive after five years of study two degrees that ordinarily require six years of work if earned separately.

## Alcoa Anti-Trust Suit Ends

June 2, 1950, saw the end of the Aluminum Co. of America anti-trust case, which has been in the courts for more than 13 years. Judge John C. Knox, chief judge of the district court for the Southern District of New York, filed an opinion deciding all outstanding issues in the suit. The decision establishes the legality of Alcoa's present position in the postwar market.

The Dept. of Justice request that Alcoa be required to sell some of its plants and facilities was turned down, the court holding that price domination had not been established. Alcoa's purchase of the Government-built St. Lawrence smelting plant was sustained, and title will go to Alcoa. The plant will be

put into operating condition immediately, the company indicated.

Alcoa's patent structure and royalty terms were upheld, the court denying contentions that Alcoa's patents dominated the industry and that the company should not be allowed to collect royalties from its competitors.

Holders of Alcoa and Aluminium, Ltd., stock in substantial amounts are required to sell their stock in either company. This will be carried out over a liberal period of time, yet to be worked out with the court. The court retains jurisdiction of the case for five years more to enable the Government to petition the court for further relief if at any time within that period the competition with Alcoa should become uncertain or ineffective.

## AIME to Meet in Mexico City

The 1951 Fall Meeting of the AIME will be held in Mexico City in October, it was voted by the Board. The invitation was tendered at the annual meeting last February by Ing. Raul de la Pena, director general of the Instituto Nacional para la Investigacion de Recursos Minerales. Several other societies covering the mineral technology field also have been invited to participate by Mr. de la Pena.

This will be the first AIME meeting to be held outside of the United States since that held in Mexico City in November 1936. A good automobile road is now open from the border to Mexico City, and frequent airplane service supplements railroad accommodations. A few technical sessions will be arranged, but the social features will no doubt dominate, and several field trips of professional, scenic, and historical interest are planned. The dates in October remain to be fixed.

Decision was also reached by the Board on several other meetings. The Annual Meeting for 1951 already had been arranged for St. Louis, Feb. 18 to 22, with the Jefferson Hotel as headquarters. The 1952 Annual Meeting will be back in New York City, Feb. 17 to 21, with the Statler as headquarters, but the banquet will be held at the Waldorf-Astoria, Feb. 20, 1952. The Fall Meeting in 1952 will be held in Chicago in connection with the Centenary of Engineering being arranged by the American Society of Civil Engineers to commemorate its 100th anniversary.

In 1953 the Annual Meeting will be held in Los Angeles, Feb. 15 to 19, with the Statler Hotel as headquarters.

## Metals Transactions Available

Transactions of the Metals Branch, AIME, for 1949 are now available. The price to AIME members is \$3.50 and to nonmembers, \$7.00. After Jan. 1, 1951, the price of this volume will be \$7.00, less 30 pct for members, and \$7.00 for nonmembers.

Mining and Petroleum transactions are also available at the same prices. The transactions are the technical material and articles, discussions, and technical notes contained in the transactions sections of the specific AIME Journals. Also included is an index.

This bound volume of transactions provides a permanent and continuing record of technical developments in the various fields covered by the activities of AIME. The attractively bound volumes will enhance anyone's technical library, and will serve as a ready and permanent technical reference.

Orders accompanied by checks may be sent to American Institute of Mining & Metallurgical Engineers, 29 W. 39th St., New York 18, N. Y.



# Flow and Velocities of

## Air and Waste Gases

### In Open Hearth Furnaces

by H. V. Flagg

**A**N exhaustive discussion of the flow of combustion air and waste gases through a regenerative open hearth furnace system would require an immense amount of experimental work to supply the necessary data. Many opposing, contradictory, and constantly changing influences are present that make positive analysis of the system difficult, if not impossible. Immense quantities of air and gases are moved into and out of the furnace by forces of such small magnitude that they defy exact measurement. Volumes are changing constantly in line with the changes in temperature occurring at every step in the process, starting with the entrainment of combustion air from the atmosphere, through its passage through the checker, its entry into the furnace, the development of the melting flame, the withdrawal of the waste gases from the furnace through the checker, and finally the discharge into the atmosphere. Exact information as to the temperatures of either air or waste gases is not available; and careful technique and procedure are required to arrive at even partial temperature information.

As a result of the complexity of these forces, no comprehensive presentation of the flow of gases through the open hearth system is available. Wm. C. Buell, Jr., made rational analyses of the problem in his book: *"The Open Hearth Furnace,"* on the basis of assumptions of temperatures to be expected at critical points according to heat balances and known process temperatures. Buell emphasized repeatedly the difficulty of establishing exact values for temperatures of gases in the path through the open hearth process. Without such values, no reasonable values for velocities can be calculated. Furthermore, any calculation of gas velocities made on the basis of flowing volume of gases and cross-sectional areas is made on the presumption of uniform flow over the entire area. It is extremely doubtful whether such

presumption can be made. Observation of the scouring effects of gases on refractories in relatively unrestricted areas after a furnace campaign will supply evidence of variation in gas velocity over those areas, which will question the usefulness of velocity data.

Furnace operators, in view of the difficulty of arriving at exact information concerning gas flows, study carefully the points of failure in the furnace system and make adjustments in furnace lines to alleviate the condition causing the failure. Unfortunately a change made to ease a condition at one point may have the effect of setting up a point of weakness at some other location, so the effect may be harmful rather than helpful. Coupled with the fact that long periods of operation are required to establish conclusively the effects of furnace changes, furnace operators, consequently, are reluctant to proceed with indicated changes and are cautious in accepting new ideas.

For the purpose of this discussion, a designation of certain critical areas in the open hearth furnace system will be used, as shown in fig. 1.

- (A-1) The transverse area at the center of the furnace between the fore-plate line and the roof.
- (A-2) The transverse area at the restriction caused by the "knuckle" and the "monkey-walls". This area influences gas flow both into and out of the furnace laboratory and is the area of first importance.
- (A-4) The vertical transverse area above the bridgewall crests.
- (A-5) The vertical transverse area over the downtakes. On open end, fixed fuel furnaces using water cooled burners and no dog house, A-5 and A-4 are practically identical.
- (A-6) The combined horizontal cross sectional area of the air uptakes.
- (A-9) The combined vertical areas of the slag pockets looking at the fantail entrance.
- (A-10) The combined cross sectional areas of the entrance to the fantails.

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*H. V. Flagg is Combustion Engineer of Armco Steel Corp., Middletown, Ohio. This paper was presented at the 1950 Open Hearth Conference in Cincinnati.*

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- (A-11) The combined areas of the entrance to the checkers above the bridge-walls.
- (A-12) The combined areas of the exit flues from the checkers on the stack side.
- (A-13) Area of air inlet duct.
- (A-16G) The area of the flue from the gas checker.
- (A-16A) The area of the flue from the air checker.
- (A-17) The area of the stack flue.

The critical areas fall naturally into two classifications. The areas A-1, A-2, A-4, A-5, and A-6 affect the flow of air to the furnace laboratory, the flow of gases across the hearth, and the discharge of gases from the furnace; while areas A-9 to A-17 are critical only with regard to the flow of gases from the furnace to the stack. The volume of gases leaving the furnace is approximately 20 pct greater than the volume of combustion air entering the furnace on the basis of normal pressure and temperature while the temperature levels are much higher, so that any area which is adequate for outgoing gases will be amply sized for incoming air.

The area A-1, the cross sectional area across the center of the furnace, is representative of the area through which the flame gases must pass across the hearth. Hence it influences the velocity of the flame gases. The length of time permitted for development of the flame and the consequent heat transfer to the charge is influenced considerably by velocity of the gas stream, or by the area A-1. The area A-2 at the *knuckle* and *monkey-walls* is recognized as the dominant area in the entire open hearth system. If area A-2 is considered as unity, the relative area for fixed fuel furnaces should be between 1.7 and 2.0, and for producer gas furnaces somewhat larger, say between 2.25 and 2.50. If this area is too large, or, in other words, if the roof is too high, more area is provided for heat loss from the furnace laboratory (where the balance is always in a narrow margin) and control of the gas stream is diminished. If this area is unduly restricted, gas contact time is shortened and refractories consumption is increased.

The velocity of gases across the hearth in a producer gas furnace probably is more or less uniform over the entire area at A-1 since the fuel and air streams both enter the furnace at relatively low velocity. This is not true in a fuel oil furnace where the atomized fuel stream enters the throat in a constricted stream at extremely high velocity. Condition at the firing end is that a slow moving blanket of air tends to hug the roof while a high velocity jet of fuel is directed toward the hearth. The injection effect of the fuel stream, coupled with the turbulence set up by the two streams moving at different velocities, tends to draw combustion air from the overlying blanket in such manner that flame development may be rapid or slow, according to the velocity and direction of the incoming air stream. As flame development progresses, the difference in velocity between the fuel and air streams becomes less and less until finally the velocity at the outgoing bridgewall should be practically uniform over the entire A-2 cross section.

It is entirely possible that the lines and areas of the throat may be opened up enough that a

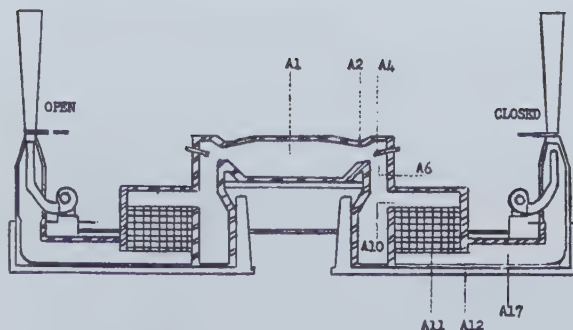


Fig. 1—Critical areas in an open hearth furnace.

considerable proportion of the air blanket may pass entirely through the furnace without involvement in the combustion process. This will have the effect of increasing the excess air in the flue gases and of robbing precious heat from the hearth where the margin between requirement and potential is always narrow. In such cases, a strict adherence to the principle that air supply should be restricted to maintain say 3 pct oxygen in the outgoing gases will mean that insufficient air will actually be available for sharp combustion; and perhaps as much as 6 pct oxygen may be needed to produce a sharp flame. The inevitable consequence of such practice will be higher fuel consumption and a slower furnace.

The area A-2 at the knuckle must always be a compromise between the restriction needed at the throat to produce the desired flame development and the wide open areas needed to permit the discharge of waste gases from the hearth with least possible restriction and resultant destruction of refractories.

The tendency in recent years has been to consider that little constriction in throat lines was necessary on fuel oil fired furnaces, and knuckle and monkey-wall restrictions have been reduced or eliminated in the interest of providing freer exits for waste gases to get longer furnace life and lower rebuild cost. It may well be that the slower melting and higher fuel consumption resulting from opening up the throat areas may justify an about-face towards increased constriction at the A-2 area. One reservation should perhaps be made with regard to concentrating attention on the A-2 area in that the vertical areas back of this area and the down take areas may have sufficient influence on incoming air to render changes in the A-2 area ineffective.

The vertical area A-4 over the bridgewalls is the area through which the outgoing gases must pass to enter the down takes. If this area is unduly restricted in the effort to properly direct the incoming air stream, the result will be rapid destruction of end walls and localized erosion of down take walls. This area should probably be at least 25 pct larger than the A-2 area and about 25 pct greater than the total down take area. The area A-5, the vertical area over the down takes, is the area A-4 less the vertical cross section area of the producer gas port or the dog house around the fuel oil burner, if used. This area should not be important on a fuel oil furnace.

The area A-6 is the total horizontal cross section of the air uptakes. On a furnace where the fuel is preheated, the area A-7 is the area of the fuel uptakes and A-8 is the sum of the two, or the to-



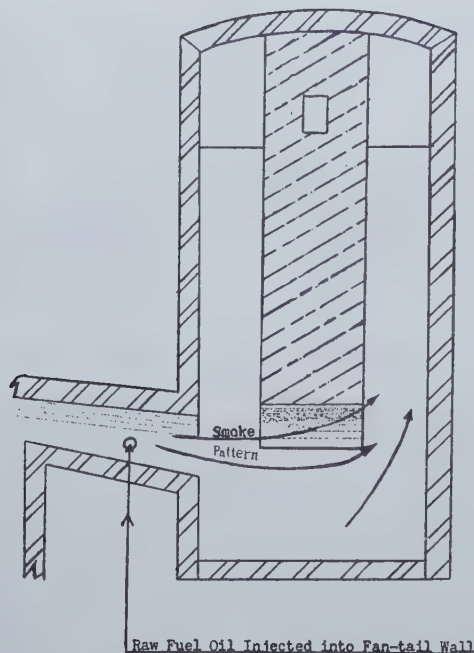


Fig. 2—Experimental fluid flow pattern, conducted by Inland Steel Co.

tal area of the down takes. A-6 and A-8 are identical on a fuel oil furnace. The area A-8 may be more significant in an open end furnace than expected.

The gas flow through the open hearth furnace system may be divided into three functions, each function being more or less independent but still being inter-dependent upon each other. The first function involves the supply of air and fuel to the furnace and includes the supply and regulation of combustion air to the checkers, its passage through the checkers and the uptakes, and finally its delivery into the furnace. The second function involves the development of the flame and the travel of the flame gases and the air blanket across the hearth. The third function involves the removal of the flue gases from the furnace, their travel through the checkers, and finally their discharge to the atmosphere.

In consideration of the first function, the motive force that moves the air into a normal furnace is developed by the chimney effect of the checkers and uptakes. All pressures in the incoming air path from bridgwall level at the top of the uptakes back to the air regulating damper are subatmospheric, or under a condition of draft. The regulating damper may be a simple saucer over an opening in the intake duct or it may be an adjustable damper in a measuring duct supplied with air from a blower. The main function of the blower in the latter case is to establish a pressure condition that will make dependable metering and air regulation possible. It is not to increase air supply as believed.

Because of the chimney effect, air current is drawn through the checkers, fantails, and slag pocket; and rises through the uptakes at a velocity depending upon the uptake areas. If the uptake areas are large, the velocity is low and the velocity energy is quickly dissipated so that the air stream will flow lazily over the bridgwall and tend to hug the roof on its path through the

throat into the furnace. If the uptake areas are made scant with regard to outgoing gas velocity, the velocity of the incoming air stream will be much higher. The result will be that sufficient energy will be developed to drive the air stream sharply toward the aprons and flame developments will be much more rapid. This somewhat hypothetical reasoning is advanced to account for the fact established in practice that opening up the furnace ends has had an adverse influence on sharpness of the furnace and on fuel consumption. This reasoning also relates to the statements that the area A-2 may not be entirely dominant and that the area A-6 may be more significant than ordinarily supposed. Experience has shown that furnace performance has been noticeably different after a 50 pct increase was made in uptake area by removing dog houses while the throat area A-2 remained the same.

The function of gas flow over the hearth has been discussed, but additional comment is indicated concerning removal of the gases from the furnace. The temperature of the gases will be increased approximately 1000° F in their passage across the furnace, which will increase their volume by about 40 pct. This increase in volume coupled with the velocity energy of the fuel and air streams tends to create a condition of pressure at the outgoing end, which must be overcome by the draft supplied by the outgoing stack. The level of pressure to be maintained in the furnace and the regulation of the draft by which the pressure level is maintained are recognized as being important in open hearth furnace operation. Excessive furnace pressure causes undue destruction of furnace refractories and backs up on the combustion air supply with the consequent adverse influence on flame development. Too much draft, on the other hand, draws in unwanted cold air through furnace openings, which not only robs the hearth of precious heat but tends to cool outgoing gases so that heat exchange in the checkers is affected adversely.

The third function, that of removal of gases from the furnace, involves the development of sufficient draft to overcome the chimney effect of the checkers and downtakes and to draw away the gases from the furnace as produced. The areas A-11 at entrance to the checkers, A-12 at exit from checkers, and A-16 and A-17 in the stack flues are important in connection with outgoing gases. Buell specified velocities of 15 ft per sec at flow temperatures for these areas. Pressures existing in the ancillary system are never static, varying over reversal periods according to temperature swings and also varying as the furnace campaign moves on and dust deposits build over the checkers and obstruct gas passage. As a result of constant fluctuation of draft in the outgoing flues, the pressure condition in the furnace tends to fluctuate accordingly. The organization of draft control to compensate for such fluctuations (in light of the sensitive forces involved, the relatively long distances, and the opposing forces of draft in each direction) requires careful engineering with sensitive and powerful instrumentation.

Conditions of furnace layout may have a critical effect on gas and air flow, even though areas may be ample for reasonable velocities. A demonstration was made recently in a Chicago plant,



which indicated such a condition. Raw fuel oil was injected into the incoming air stream through a fantail wall and observations were made of the path of the resulting smoke. All of the smoke carried across the slag pocket and rose through the far uptake, as indicated in fig. 2. This supplied strong evidence that a disproportionate part of the combustion air supply was concentrated on one side of the furnace. Such a condition would inevitably result in an unbalanced flame development. The remedy planned is to raise and round off the fantail roof under the uptake wall and lower the arch that supports the dividing wall between the uptakes, so as to trap part of air supply into the near uptake. In addition to this rather extensive change, any restriction that could be made in uptake area A-6 would tend to improve distribution of air.

Another instance of the effect of layout was cited by Buell in Vol. III in his discussion of gas and air flow through checker chambers. He pointed out that restrictions at either the fantail end, A-11, or the stack end, A-12, or both, would result in increased velocities of outgoing gases or of incoming air, or both. This would tend to spread the paths of these two currents, with the result that checker brick at the rear of the chamber would be subject to destructive heat from outgoing gases while incoming air would reach the furnace underheated.

Buell also showed diagrammatically, as reproduced in fig. 3, the effect of acutely angled approach and exit connections to checker chambers on the paths of air and gases through the chambers. With generously sized entrance and exit and straight flow lines as shown in A, fig. 3, velocities should be low and the paths of flow well-distributed. The angled entrance and exit shown in B would have the effect of restricting further the areas A-11 and A-12, and would distort the flow path as indicated. The result is that a considerable portion of the checker work, as shown shaded, would be ineffective while the remainder might be overheated. In substantiation of these ideas, Mr. Buell cited experimental work done by T. J. McLoughlin and reported by him in a paper: "The Theory and Application of Regenerative Principles in the Steel Industry," in the Proceedings American Iron and Steel Institute, 1929.

Emphasis has been placed on the need for provision of sufficient draft to keep the furnace in operation after checker deposits have built up to the point where additional draft is required. Experience has established the fact that anticipated benefits can not be obtained, since the checker dirt deposits have increased the velocity of waste gases to a point where heat exchange to the checkers is decreased and lowered air preheat slows up the furnace. This has been found true on Isley furnaces where ample draft is available.

Since the entire ancillary system is continually under a pressure condition below that of the atmosphere, air will be drawn into the system through every crack and opening. A certain amount of infiltration is inevitable, since it is impossible to maintain the system air tight in the face of inherent temperature changes. However, sustained effort should be directed toward holding the amount to a minimum so that a com-

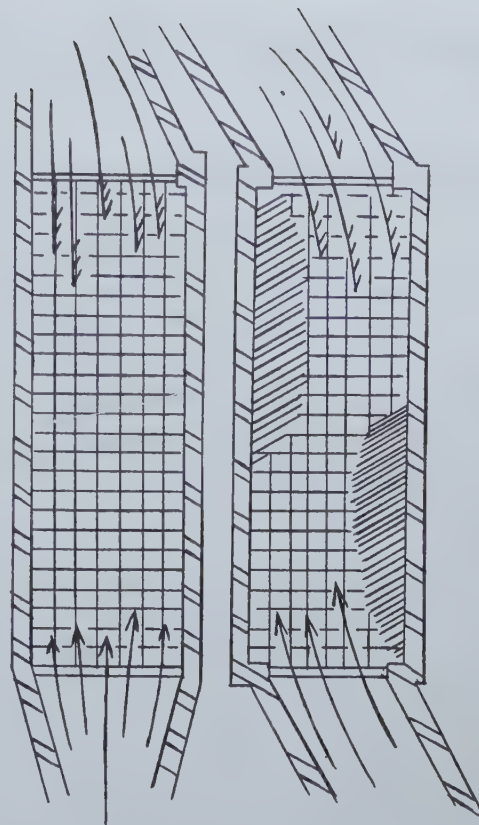


Fig. 3—Influence of angularity of fantail flues and connections. (From "The Open Hearth Furnace," Vol. III, by William Buell)

fortable margin of controllability can be maintained and unnecessary heat losses be eliminated. Infiltration may account for as much as 50 pct of the combustion air supply, with the result that the measure of control left in the remaining 50 pct may be inadequate. Infiltrated air has a double barreled influence adverse to good furnace operation since the greater part occurs between the top of the checker and the top of the uptakes, so that infiltrated air is always cold. This reduces air preheat on the incoming end and chills flue gases on the outgoing end. Thus, infiltration has the effect of reducing the amount of heat given up to the checkers from the outgoing gases, which will mean lower air preheat on the succeeding reversal, while the effect of infiltration on that reverse will be to add cold air to the preheated air stream and further reduce air preheat. Another effect of excessive infiltration may be to increase the volume of gases to the point where draft control is sluggish and possibly even to the point where available draft is insufficient.

Emphasis has been placed on the first function, which relates to the delivery of air to the furnace. Well organized flame development is the first requisite for good melting practice. The manner in which combustion air is introduced into the throat of the furnace plays an important part in flame development. The extent to which opening up the ends of the furnace can be carried in the interest of easier gas exit must be governed by the requirements for sharp flame development.



# Open Hearth Bath Temperature Measurement and Control

by J. A. Creighton

SINCE May, 1949, at Bethlehem Steel Co.'s Lackawanna plant, No. 3 Open Hearth shop, all tapping temperatures have been controlled by platinum: platinum-rhodium thermocouples, used with high speed electronic recorder. This shop consists of six furnaces tapping 220 tons and the steel made is mostly strip mill steel of 0.08 pct max carbon. Practically all heats are lanced with oxygen from 0.15 to 0.25 pct carbon down to 0.04 to 0.05 pct carbon. Practice is to take one pyrometer reading just before lancing and a second reading just before manganese addition to the furnace. A schedule of fuel rate during the blow and up to tap is followed to get the desired tap temperature. The aim is a minimum tapping temperature that will give a heat free from any skull. Many of the grades made call for complete killing by aluminum in the ladle and the tendency is to get those heats too hot (because of the heat pickup in the ladle) unless the heat is tapped at a temperature which the ordinary melter would hardly dare to use. The pyrometer gives him confidence to take the heats below normal tapping ranges and an alibi if needed. The reduced temperatures on this grade of aluminum-killed steel is felt to have been one of the best contributions of pyrometric control.

Lancing with oxygen adds to the problem of achieving the proper tapping temperature. During the oxygen blow it is possible to pick up from

0 to 90° F in temperature, depending on how much fuel is used. The operation works to a scheduled fuel rate, based on the initial temperature, and the heat is usually somewhere near the right point when the second reading is taken.

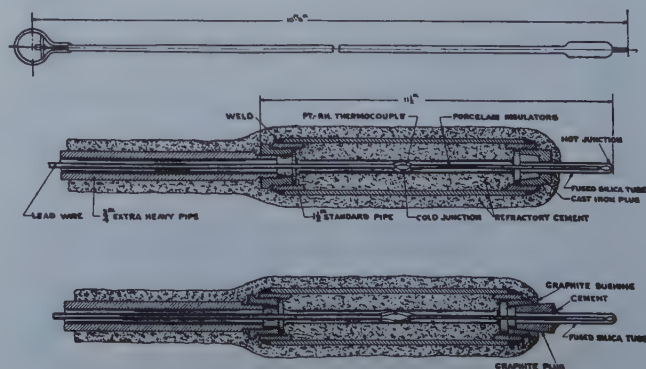
Table I gives the desired tapping temperatures, based on steel grades. These have been arrived at by experiment and experience.

Table II shows the schedule of fuel rates to be used during oxygen blow. These fuel rates are based on the carbon content of the bath at the start of the blow.

As to results obtained from pyrometric control experience is that skulls have not increased or decreased. Since working to a lower average temperature, it is not surprising that skulls have not decreased.

Mold life has definitely increased. Coincident with the use of the pyrometer, the mold life on

Fig. 1—Thermocouple assembly for temperature measurement of liquid steel baths.



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TABLE I

## Desired Tapping Temperatures by Grade of Steel

Ladle Carbon, Pct	Deoxidation	Tapping Temperature Aim, °F
Under 10	Rimmed	2890
Under 10	Aluminum Killed	2840
10 to 20	Rimmed	2880
10 to 20	Killed	2860
20 to 30	Killed	2850
30 to 40	Killed	2840
40 to 50	Killed	2830

the 24 x 54 in. mold, which is largely used at No. 3 Open Hearth, has increased from 70 to 88 pct. Realizing that variations in mold life are affected by a number of conditions this substantial increase is quite significant.

Stool life has increased, coincident with the use of the pyrometer. The number of pounds of stools per ton of ingots has gone down from an average of 15.3 to 11.7 lb per ton. For the past three months it has averaged 9.8 lb per ton. Other

TABLE II

## Fuel Rates Used During Oxygen Blow, Based on Carbon Content at Start of Blow Temperature Increase, °F

Gal Oil per hr	From 20 C	From 15 C	From 10 C
0	20	10	0
50	25 to 30	15 to 20	5 to 10
100	35 to 40	25 to 30	10 to 15
150	45 to 50	30 to 35	20 to 25
200	50 to 55	40 to 50	30 to 35
250	60 to 65	50 to 55	35 to 40
300	65 to 70	60 to 65	45 to 50
350	75 to 80	65 to 70	55 to 60
400	85 to 90	75 to 80	65 to 70

things have affected these results, but the tendency is there.

Pouring practice at No. 3 Open Hearth has improved greatly coincident with the use of the pyrometer. For the eight months prior to May, 1949, the average pouring practice was 89.7 pct. For the eight months' period after May, 1949, the average was 94.4 pct. For the past two months the average pouring practice is 96.8 pct. This improvement is attributed to the elimination of the hotter heats. Stool stickers and mold stickers also have decreased materially.

As to quality of steel produced, no concrete data are available, but correct pouring temperatures and better pouring practice is believed to result in improved quality. On higher carbon heats, such as rails and high carbon forging heats, it is believed the effect on quality will be more pronounced. At present pyrometric control is being installed in No. 1 and No. 2 Open Hearths Shops where the higher carbon heats are made.

As to the actual use of the pyrometer, the technique of manipulation and maintenance of the equipment determines its success. An observer who comes under the Metallurgical Dept. inserts the pyrometer in the bath, assisted by the first helper. The maintenance of the equipment is the responsibility of the metallurgical department. The melter takes the reading from the recording chart. The accuracy of readings is about  $\pm 10^\circ$ . Sometimes a bad reading is obtained, but such readings usually are indicated by irregularity in the curve on the chart and discarded. Fig. 1 shows a sketch of the thermocouple. The couple and silica tube are removed after each reading and replaced with a new assembly. The graphite-plug type is preferred. The cost of labor and material for each reading is somewhere around \$1.13.

Experience has proved that the platinum thermocouple, if carefully maintained and operated, can be used successfully for routine bath temperature control. Its use is believed to have improved mold life, stool life, pouring practice, and steel quality.

## Commercial Slag Uses Increase

THE development of commercial markets for iron blast furnace slag has been rapid in the United States during the past 20 years, although the product has been used for road construction and for ballast during the early part of the century. Some foreign countries are reported to have used the material for various purposes much earlier.

Of the 32,824,000 tons of slag produced as a byproduct of the iron and steel industry during 1947, about 19,582,000 tons or about 61 pct was used commercially. This tonnage was valued at \$19,526,000. Used in roads and streets other than in concrete and bituminous work was 27 pct, railroads used 21 pct for ballast, 9 pct was used in concrete block and other concrete products, 8 pct in portland cement concrete construction, five in cement manufacture, 2 pct in roofing ma-

terials, and the remaining 6 pct for miscellaneous purposes.

There are 62 plants for processing iron blast furnace slag, producing four general types of commercial slag: 1—Screened air-cooled, used chiefly as aggregate and railroad ballast; 2—Unscreened air-cooled, employed in base courses for roads and as fill; 3—Granulated slag for fill in highway pavement base courses and in the manufacture of cement; and 4—Lightweight slag, used in molded concrete products.

Some slag serves as a chemical or ceramic raw material in producing mineral wool and cement, as well as in the manufacture of some types of glass, ceramic ware, and in soil treatment. The history and development of the slag industry are described in Bulletin 479 (price, 75c), of the National Bureau of Standards, Washington, D. C.



# Oxygen for Carbon Reduction And Temperature Pickup

by E. H. Reyer

**O**XYGEN injection as a standard practice during periods when extra production is needed has been adopted by Keystone Steel & Wire Co., Peoria, Ill. The open hearth shop contains three 170-ton furnaces firing a mixed fuel of 65 pct natural gas and oil atomized with steam, and fired at a rate of about 70,000,000 btu per hr. The charge is all scrap and cold iron plus broken cast iron molds or other pig iron substitutes. Types of steel made are 0.04 to 0.25 pct carbon rimmed and 0.08 to 0.90 pct carbon semi-killed and killed.

The high pressure oxygen supply system consists of four large tube trailers, each having a capacity of 45,000 cu ft of commercial high purity oxygen. The trailers are connected individually to a set of pressure reducing regulators, allowing for the adjustment of the pressure to 110 psi static pressure. Automatically controlled valves permit each trailer to be used and operated independently, thus insuring a continuous supply of oxygen. Oxygen is conducted through a 2-in. pipe line that extends the length of the shop.

At each furnace is a station control unit consisting of a throttle valve and a quick shutoff valve. A 60 ft length of high pressure heavy duty hose serves as a flexible link between the station control unit and the furnace. The oxygen is injected into the furnace through a 1-in. pipe at the rate of about 450 cfm. About 70 ft of pipe are consumed during a complete injection period.

Oxygen injection is started shortly after the heat is under cover, following a burnt lime addition. This lime addition serves to confine to the bath the temperature generated by the oxygen. Injections are continued intermittently up

to tap time, depending on carbon drop, temperature pickup, and action of the bath. Cold metal practice differs from hot metal practice in the respect that just enough pig iron or pig iron substitute is charged to melt and work the heat and to finish at the desired analysis. The use of oxygen speeds up the reaction so that less iron can be charged than with a non-oxygen practice.

There are several advantages to this particular use of oxygen. Rapid decarbonation is accomplished during the injection period, and associated with the practice is the rapid oxidation and elimination of impurities. Some consideration has been given to the possibility that it is a prevailing influence on the removal of sulphur. Sulphur residuals average 0.5 to 0.10 pct lower on oxygen vs. non-oxygen heats with comparable charges. The practicability of its use as an oxidizing agent to replace iron ore or mill scale is evidenced by the fact that its reaction is exothermic. This is a distinct advantage in finishing heats very low in carbon.

Higher tonnages can be maintained with existing equipment. For example, during the summer of 1949, the demand for steel was low, so a total of 375,000 cu ft of oxygen were used in July. As steel demand rose, the oxygen was increased until consumption totalled 2,000,000 cu ft in October. Production in July averaged 12.09 tons per hr vs. 14.5 tons per hr in October; while the Btu per ton average for July was 4,738,000 vs. 4,113,000 for October. These tonnage figures are based on the number of hours in the month, making no allowance for fettling time, bottom delays, or masonry repairs.

The furnaces are run at different pressures. When a furnace gets older and just the least bit choked up, normal pressure would be  $\frac{3}{4}$  in. of water. While using oxygen, it may increase to five or six. The entire increase in production is

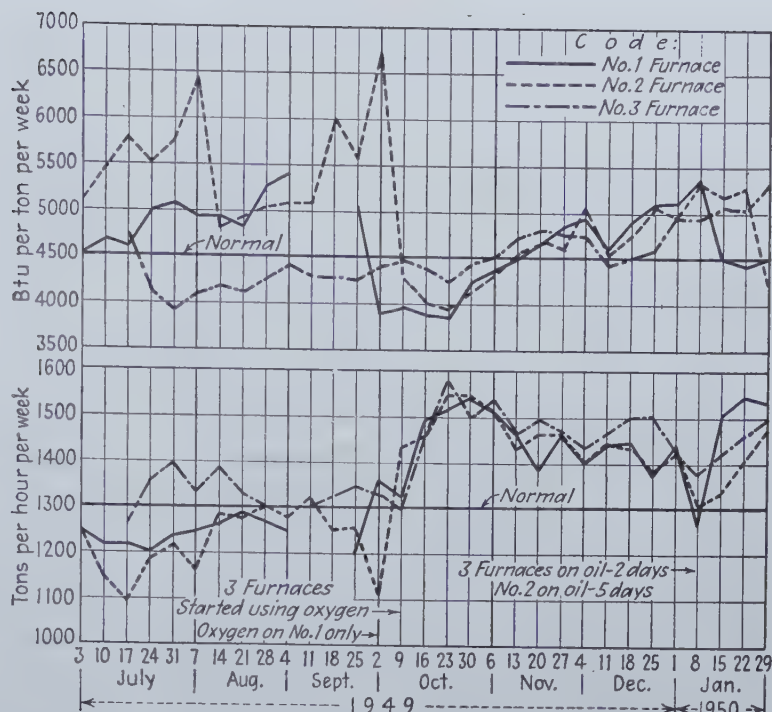
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Details of an open hearth campaign using oxygen for carbon reduction and temperature pickup.



not entirely attributable to the use of oxygen. The Scrap Dept. has lowered charging time considerably, but a faster charging time was required to keep up with the oxygen.

The effect on sulphur, a drop of as much as 8 points, is partly the result of the increased temperature during the time of the lime boil. Lime, it has been found, shapes up better at the higher temperatures and with more action. At least some of the fuel is on at all times, depending on the stage the heat is in. Some plants shut the fuel off when working up the heat with the oxygen, and find it is easy to get lime into solution quickly. It is desirable to maintain the proper pressure to operate the furnace. Automatic dampers in the boiler stack are governed by pressure in the furnace.

One of the more important aspects of the use of oxygen is the fact that now 14 to 15 tons per hr can be obtained from a furnace more than 250 heats old. Such a furnace formerly produced around 11½ tons at this age. A recent example was the No. 3 furnace, which was producing more

than 14 tons per hr at the time of shutdown at 411 heats.

A limiting factor in the use of oxygen is the greater erosion of brick in the furnace. Waste gases are carried away by an induced draft fan, operating through a waste heat boiler. The fan capacities were not designed for the extra volume of fumes and gases generated by the oxygen, which necessarily increases the pressure on the furnace. This pressure at higher temperatures effects brickwork to some extent.

The overall economics of oxygen injection are as yet somewhat vague. The direct costs average around 28¢ per ton; that is, oxygen plus pipe costs. To this must be added the extra costs of brickwork, which in turn are counterbalanced to some extent by the savings in fuel plus the added efficiency of older furnaces.

Some added equipment and research probably will improve oxygen practice but the most important factor in maintaining the ultimate tonnage with the least effect on furnace life is an experienced and conscientious first helper.

## Zinc Alloy As Strong As Brass

A NEW alloy composed principally of zinc, with small quantities of copper and beryllium added, has approximately the same strength and electrical properties as brass, and is said to be considerably cheaper than brass. Called "Zncube" (pronounced "zin-cu-be"), the alloy has about eight times the useful strength of any zinc alloy now in use, according to Dr. R. H. Harrington, of General Electric Co.'s Research Laboratory, who developed the new material.

A 12-in. strip of ordinary zinc 1/16 in. thick will sag slowly from its own weight when supported horizontally from one end. The new alloy however, has a springy, resilient quality.

Among the applications where the more economical Zncube might be substituted for brass are lamp and fuse sockets and bases, panels, containers, mild springs, and many forms of hardware. The alloy can be machined and soldered, and will resistance weld quite easily.



# Ferrochromium from

## Low Grade

## Chromite Ores and

## Concentrates

by F. W. Wessel

and R. T. C. Rasmussen

**R**ESearch at the Northwest Electrodevelopment Laboratory on electric smelting of domestic chromium ores or concentrates was to learn the smelting characteristics of the domestic materials. Also, the research sought to determine whether ferrochromium of compositions acceptable for at least part of American industrial requirements can be produced from chromite of the low chromium: iron ratio characteristic of United States ores by usual electric furnace smelting procedure. The latter objective is based in part upon the premise that ferrochromium of lower chromium content than specified in present standard grades can be used in the manufacture of some alloy steels without serious technologic difficulties. The most important domestic reserves of chromite are in the Sweetgrass-Stillwater complex of south central Montana. Concentrates from the Mouat-Sampson deposit of that area were the subject of all tests reported. Production of high carbon ferrochrome is the principal topic, but a few tests on decarburization and further refining also are discussed.

Consumption of crude chromite in the United States has been increasing steadily since World War II and reached 236,017 short tons for the first quarter of 1949.<sup>1</sup> Domestic production of chromite from 1935 to 1940 amounted to 11,000 tons,<sup>2</sup> and for 1946 to 1948, 8,500 tons;<sup>1</sup> production for the first quarter of 1949 was 152 tons.<sup>1</sup> Domestic producers thus account for only a fraction of 1 pct of normal domestic needs.

In the first quarter of 1949, metallurgical uses of chromite—48 pct of the total consumption—were supplied by imports from: U. S. S. R., 37 pct; Turkey, 28 pct; New Caledonia, 18 pct; Southern Rhodesia, 13 pct; and Yugoslavia, 4 pct.<sup>1</sup>

Domestic deposits, though of significant size, are not used metallurgically to any extent because they are of lower grade and higher iron content than the importable material. Principal domestic sources of chromite are located in Montana, California, and Oregon; less important deposits occur in Alaska, Washington, Idaho,

Wyoming, Pennsylvania, Maryland, and Georgia. Typical analyses of chromium ores from various sources are given in table I.

Since chromite supplies are vulnerable in times of war, and to some extent in times of peace by economic action, the Bureau of Mines has been investigating domestic resources and the development of methods for their utilization. Experimental programs have been or are being carried out on the following phases of the problem:

- 1—Beneficiation by ore dressing methods.
- 2—Use as refractory material.
- 3—Chemical beneficiation.
- 4—Direct addition of chromite concentrates in the manufacture of stainless steel.
- 5—Preparation of pure chromium metal by electrolytic methods.
- 6—Smelting in the electric furnace.

Ore dressing methods,<sup>6, 7, 8</sup> while successful in up-grading ores to some extent, are of limited value because the chromium mineral is picotite, chromohercynite, or picrochromite. Almost all the iron together with the greater part of the alumina and magnesia are concentrated along with the chromium. The concentrates made are generally somewhat inferior to imported ores with respect to  $\text{Cr}_2\text{O}_3$  content, and much inferior with respect to chromium: iron ratio.

Extensive testing of chemical beneficiation methods failed to develop an economically attractive process.<sup>5, 9</sup> Promising results, not yet published, were obtained in tests at the Northwest Electrodevelopment Laboratory on the manufacture of stainless steel from Cle Elum ferromanganese and Oregon chromite concentrates in the arc furnace. Such direct use of chromite ore or concentrates in the manufacture of stainless steel is practiced industrially, but not generally. Production of pure electrolytic chromium metal is still in the pilot plant stage.

Previous work on direct smelting of domestic chromites has not been extensive. Koster<sup>7</sup> smelted chromite of 1.66 chromium: iron ratio with sand, coal, and fluorspar, in an induction furnace, making a metal of 55 pct Cr, 33 pct Fe, 2.5 pct Si, and 8 pct C. Knickerbocker, Royer, and Evans,<sup>10</sup> using an ore of 25.6 pct  $\text{Cr}_2\text{O}_3$ , 15.4 pct, FeO, and having a chromium: iron ratio of 1.52, made metal of 53.7 pct Cr, 35.1 pct Fe, and

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7.7 pct C, in a chromite-lined electric arc furnace. A similar heat on concentrates of 40.4 pct  $\text{Cr}_2\text{O}_3$  and 19 pct FeO yielded ferrochromium of 54.8 pct Cr and 33.3 pct Fe.

The intensive exploration and development program carried on during World War II indicated that the nation's largest reserve of chromite lay in the Stillwater complex, in Stillwater and Sweetgrass counties, Montana. Supplementary sources, of tonnage, are found over a wide area of the Sierra Nevada and the Siskiyou Mountains, and in beach and river sands and gravels in California and Oregon.

The Montana chromite used was a concentrate produced by the Defense Plant Corp., mill at the Mouat deposit. Analyses of the two lots of this material received for use in the investigation are shown in table II. The lots consisted of minus 20-mesh material, with less than 1 pct moisture.

Two available reductants were used: A sub-bituminous coal from the Coos Bay, Ore., area, and a char from this coal made by driving off much of the volatile matter in a rotary kiln. A coal similar to that used is mined in the Red Lodge, Mont., field within 50 miles of the chromite deposit, and a somewhat better coal is available in the Bull Mountain, Mont., field, some 125 miles to the north.

Preliminary crucible tests were made in a gas-fired pot furnace. The silicon carbide crucibles employed in most tests proved satisfactory for only one phase of the program, but no other crucible material was found (except graphite or clay-graphite) that would not fail at some time during a test. Of the various types of silicon carbide crucibles tried, those lined with fused alumina came the closest to meeting general requirements.

The crucible tests had as their purpose: 1—The establishment of the composition of a slag having a reasonable melting temperature and good working properties; 2—the selective reduction of iron from the chromite concentrate; and 3—as it became apparent that the silicon carbide crucibles were not suited to selective reduction charges, finding of a satisfactory crucible material. Efforts toward the two latter aims were unsuccessful. An area of satisfactory slag composition was found in the range of 40 to 45 pct  $\text{SiO}_2$ , 15 to 20 pct  $\text{Al}_2\text{O}_3$ , and 35 to 40 pct CaO plus MgO. A second area, not quite as satisfactory, was found at 50 pct  $\text{SiO}_2$ , 30 pct  $\text{Al}_2\text{O}_3$ , and 20 pct CaO plus MgO.

The major part of the data was developed in batch tests in a single-phase, manually controlled Swindell-Dressler arc furnace of 500-lb nominal capacity for steel. Two top electrodes of 3-in. diam graphite were inserted through openings in the monolithic sillimanite roof of the furnace. The walls and hearth of the furnace were lined with magnesite refractory for most of the tests. Chrome refractory walls and a silica hearth were installed later for several acid smelting tests.

An operating procedure was developed and generally adhered to thereafter. After preheating the furnace with a gas torch, a quantity (usually 1.5 lb) of metallurgical coke was placed on the hearth, and the electrodes were lowered until an arc was struck on the coke. Within 5 min, sufficient heat had been generated to permit charging. A molten pool soon formed around the

Table I. Typical Analyses of Chromiferous Materials

Source	Material	$\text{Cr}_2\text{O}_3$ , Pct	Ratio, Cr:Fe
<b>Imported chromites:<sup>4</sup></b>			
Russia	ore	51.2	3.3:1
Turkey	concentrate	49.5	3.1:1
Transvaal	ore	43.9	1.6:1
Rhodesia	ore	47.9	3.0:1
Rhodesia	ore	46.9	2.6:1
Sierra Leone	ore	41.0	2.9:1
New Caledonia	ore	52.7	3.3:1
Cuba	ore	44.9	3.1:1
Cuba	ore	36.9	2.3:1
<b>Domestic chromites:</b>			
Antelope, Mont. <sup>5</sup>	concentrate	36	1.3:1
Benbow, Mont. <sup>5</sup>	concentrate	41.3	1.51:1
Castra, Calif. <sup>4</sup>	concentrate	42.0	2.5:1
Coquille, Ore.	concentrate	38.9	1.41:1
French Hill, Calif. <sup>3</sup>	ore	38.7	—
Gray Eagle, Calif. <sup>4</sup>	concentrate	46.0	2.8:1
Kenai, Alaska <sup>3</sup>	ore	42.5	—
Mouat, Mont.	concentrate	37.4	1.41:1
Seiad, Calif. <sup>3</sup>	concentrate	52.8	1.97:1

electrodes, surrounded by unsmelted charge; as smelting progressed, this pool became larger, until near the end of the smelting period only a small quantity of unsmelted material remained on the banks. This was raked into the bath, and smelting continued until the flame color of the burning gases changed from orange to yellow, and a fine white silica fume began to evolve. During the foregoing, charge was added periodically, a few pounds at a time. Dry-top conditions prevailed for a time after each charge addition, after which the surface of the pool again became molten.

The metal produced during smelting apparently dropped to the hearth in a solid or plastic condition. Rate of power input, which up to the close of the smelting period was about 60 kw, was increased to 80 kw, and the bath heated until a clean spoon sample of metal could be obtained, or until the evolution of flaky particles of white fume (reported by Koster)<sup>7</sup> had continued for about 30 min.\* Slag and metal then were poured

\* Analyses of two samples of this fume showed the major constituents to be silica and magnesium oxide.

together into a conical, cast iron ladle, and allowed to cool. When subsequently removed from the ladle, slag-metal separation was uniformly good.

The first consideration in the arc furnace smelting program was the application of the data obtained from crucible testing to producing ferrochromium under a slag of fluidity sufficient to

Table II. Analyses of Mouat Chromite Concentrates

	Analysis, Pct	
	Lot 1	Lot 2
$\text{Cr}_2\text{O}_3$	39.3	37.4
Fe	18.7	18.1
$\text{SiO}_2$	9.8	6.1
$\text{Al}_2\text{O}_3$	17.2	14.7
CaO	0.7	0.2
MgO	11.7	13.7
P	0.08	0.013
S	0.01	0.02
Ratio Cr:Fe	1.44:1	1.41:1



cause no operating difficulties. A number of heats were accordingly made with charge proportions in the following range: Mouat chromite concentrate, 2000 lb; limestone, 500 to 700 lb; calcined magnesite, 75 to 0 lb; quartz, 570 lb; and Coos Bay char, 715 to 940 lb.

Magnesite was used at first to satisfy two requirements: 1—The slag should have a basicity of 1.0; 2—the slag should have the composition (neglecting chromium and iron) indicated as most favorable by the crucible tests. Experience proved, however, that additional limestone could be substituted for the magnesite, improving the economics of an industrial operation. Nevertheless, a dolomitic limestone might under some conditions be equally satisfactory.

Important quantities of magnesia were taken from the refractories by the slag, this effect being particularly noticeable when the melt was subjected to sustained heating after the smelting reactions were complete. Prolonged heating also reduced the silicon content of the metal with proportionate increase in chromium and iron. Because of magnesia pickup from the hearth, slags calculated to have a basicity of 0.9 to 1.1 actually analyzed 32 to 40 pct SiO<sub>2</sub>, 14 to 20 pct Al<sub>2</sub>O<sub>3</sub>, and 43 to 52 pct CaO, plus MgO. These slags were fluid at 1585° to 1650° C.

It is possible, considering the drift of slags toward higher lime-magnesia content, that flux additions can be so balanced as to produce such a slag, without attack on the refractory, at little or no additional cost.

After establishing charge proportions that produced a desirable slag with reasonable flux additions, a series of five smelting tests were made on almost identical charges containing enough carbon for substantially complete reduction of chromium and iron. The carbon: chromium ratio of the charge was 1.02:1 in each test. The following charge was used in three of the tests:

**Table III. Data From Five Check Tests in Swindell Furnaces**

	Range or Average	Typical Test
<b>Analyses of Ferrochromium, Pct:</b>		
Cr	47.5 to 50	49.5
Fe	35 to 40	36.9
Si	1 to 8	5.24
C	5 to 8	5.88
S	less than 0.01	0.01*
P	less than 0.1	0.093
<b>Analyses of Slag, Pct:</b>		
Cr	0.3 to 0.9	0.6
Fe	0.4 to 1.1	1.0
Recovery of Cr in Metal, Pct.	94.0 to 98.2	97.3
Recovery of Fe in Metal, Pct.	93.4 to 97.2	94.1
Rejection of S to Slag and Gases	94 to 99	98.6
<b>Slag Temperatures as Tapped, °C</b>		
Average Time of Heat, Hr	1585 to 1750	1620
Reductant Used per Ton of Ferrochromium, lb	3.34	2.97
Electrodes Consumed, per Ton of Ferrochromium, lb	2080	
Slag Weight, per Ton of Ferrochromium, lb	130	
Power Consumed, per Ton of Ferrochromium, Kw-Hr	5400	
	12800	

\* Indicates less than.

**Table IV. Results Obtained With Various C:Cr Ratios**

C:Cr Ratio	1.02:1*	0.87:1	0.72:1	0.56:1	0.41:1
<b>Metal Produced, per Ton of Concentrate, Lb</b>					
	953	716	716	544	247
<b>Analyses of Metal, Pct:</b>					
Cr	49.4	47.8	47.6	43.7	27.6
Fe	36.4	42.0	44.3	46.1	66.3
Si	4.72	0.17	0.18	0.36	0.15
C	6.2	7.4	7.0	7.0	3.9
S	0.01**	0.02	0.07	0.06	0.08
P	0.095	0.07	0.07	0.08	0.03
<b>Analyses of Slag, Pct:</b>					
Cr	0.66	3.9	6.6	8.7	12.7
Fe	0.89	1.1	1.6	3.6	4.8
<b>Cr:Fe Ratio in Metal</b>					
	1.36:1	1.14:1	1.07:1	0.95:1	0.42:1
<b>Recovery in Metal, Pct:</b>					
Cr	96.7	79.2	67.0	52.0	16.1
Fe	93.9	92.3	88.6	72.4	54.9

\* Average of five heats.

\*\* Indicates less than.

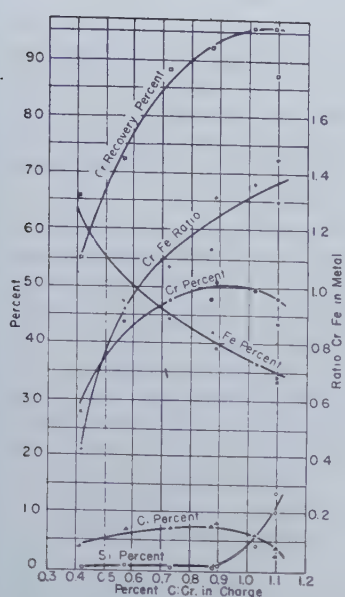
Mouat chromite concentrate, 81 lb; limestone, 28.5 lb; quartz, 23 lb; and Coos Bay char, 33.5 lb.

These tests were made to obtain average data that would be more reliable than those of a single test. For instance, it is difficult in batch tests to be sure that all the metal is removed from the furnace without tearing up the hearth, and it is impossible to judge accurately the quantity of slag adhering to the refractories after a test. All recovery figures indicated in this article, except those for sulphur, are based upon contents of the metal and slag products removed from the furnace. Another purpose of the series was to establish optimum operating conditions for smelting, with minimum cutting of the hearth refractory. Range or average data for the five tests and actual data for one of the tests are presented in table III. Recoveries of chromium and iron were generally good and fairly consistent, as were chromium and iron analyses of the ferrochromium product. Silicon and carbon contents of the alloy product varied over wide ranges from test to test. In general, increased silicon content was accompanied by decreased carbon content, as a function of operating variables.

A series of heats was then made in which the ratio of fixed carbon to chromium in the charge was varied. Neither carbon in the starting coke nor that taken from the graphite electrodes was included in the calculations. Charges consisted of 81 lb chromite concentrate, 28.5 lb limestone, and 23 lb quartz; char content varied from 28.5 to 13.5 lb by increments of 5 lb. In these heats, the metal apparently collected on the hearth in the molten state during smelting, instead of in the solid or plastic condition noted for other tests.

Using the carbon:chromium ratio of 1.02:1 as a starting point, both the grade and the recovery of chromium showed a decline with the first decrease of the ratio. The iron content increased, while iron recovery showed a slight decrease. Silicon dropped to an apparently minimum range. At each subsequent decrease in the carbon:chromium ratio, these tendencies became more marked, until, with a ratio of 0.41:1, the character of the metal produced was that of high





**Fig. 1 — Composition of ferrochromium produced and recovery of chromium expressed as functions of the ratio of carbon to chromium in charges smelted on a basic hearth.**

chromium pig iron. These data are presented in table IV. Portions of the data have been plotted in fig. 1. Apparently, at some carbon:chromium ratio between 1.02:1 and 0.87:1, silicon reduction virtually ceases. It will be attempted to determine this point accurately in future work, since it seems reasonable to suppose that this is also the point below which chromium recovery declines. Furthermore, as the curves become steeper in the lower C:Cr range, a point should exist at which some iron may be removed as metal without serious loss of chromium. Selective reduction of this sort, if flux requirements can be reduced, may make feasible the reduction of 70 pct ferrochromium from the remaining slag.

In heats in which complete reduction of chromium and iron was approximated, the silicon content decreased with increasing carbon content of the alloy. The data plotted in fig. 2 seem to show a linear relationship having the approximate empirical equation:  $\text{Pct Si} = 19.1 - 2.3 (\text{pct C})$ .

The atomic weight of carbon times 2.3 equals 27.6, which is close to the atomic weight of silicon. The relationship might be interpreted to indicate the saturation point at which all iron and chromium of the alloy are present as silicate or carbide. The question of the relative amounts of carbon and silicon to be expected in ferrochromium from a given charge seems to be governed to some extent by the power input. Those heats consuming more power yielded metal containing less silicon. The exact mechanism of control, to be studied further, is apparently important in the smelting of chromite.

A few tests were made in which decarburization was attempted by additions of chromite concentrate to the fluid metal, the primary slag having been decanted. About 20 pct silica sand was mixed with this ore-down concentrate to flux its magnesia and alumina content. Any silicon existing in the primary metal was easily removed; but carbon oxidized much less readily. Moreover, the reactions involved exhibited some degree of selectivity, iron being reduced from the chromite in much greater quantities than chromium.

In the course of one heat, the ore-down charge was added at a uniform rate over a 54-min period, and thimble samples of slag were taken at inter-

vals. Comparative analyses of the primary and final metal of the heat are in table V.

In a subsequent test, heat no. 41, a quantity of 98 pct silicon metal was added (after sufficient time had elapsed for completion of the ore-down reactions) with a view to reducing oxidized chromium back into the metal. This procedure showed some promise and will be studied further. These data are also presented in table V.

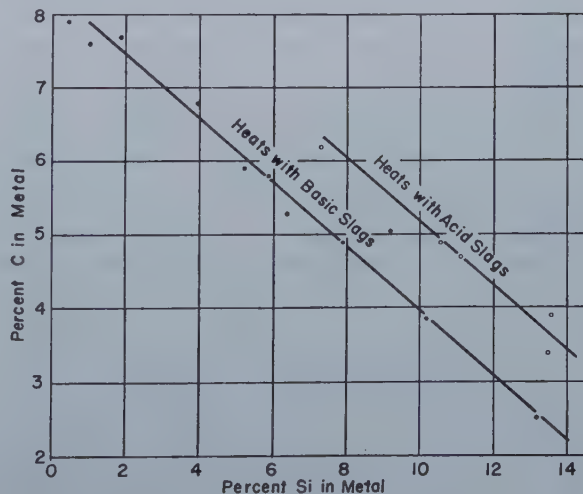
An exploratory heat, fluxed to make a slag of 50 pct silica, 30 pct alumina, and 20 pct magnesia, was made. Since the slag was distinctly acid, the charge was smaller than usual to reduce the time of residence and the consequent attack on the basic refractories. Results were not favorable.

The furnace was relined with a silica hearth, and a series of tests with both acid and neutral slags was made. The alloys produced were generally of higher silicon content and had a higher Cr:Fe ratio than those produced under neutral slags in the basic-lined furnace. Charge composition and results are summarized in table VI.

One continuous, open-top smelting test of short duration was made in a type ST Lectromelt furnace of 2000-lb nominal capacity for steel. The furnace was a 3-phase arc furnace, rated at 500-kw capacity with 4-in. diam graphite electrodes. It was lined with 9-in. magnesite brick walls and had a rammed magnesite hearth. The furnace was without a roof, its wall height was increased by means of a refractory-lined spare roof ring, and the charging door was bricked up. The electrodes are regulated automatically.

Total charge for the heat comprised a mixture of 1000 lb chromite concentrate, 352 lb limestone, 284 lb quartz and 685 lb coal. Charging was by hand shovelling whenever the operation appeared to require more charge, and the average charging rate was 158 lb of chromite concentrate per hr. Optimum power conditions appeared to prevail with a power input of 150 kw at 66 volts, phase to phase, and 1400 amp per phase.

Smelting proceeded quietly under good dry-top conditions throughout. The furnace was tapped from the single tap hole, without forward tilting, three times during the heat at intervals of about 2 hrs. Material removed average about 155 lb of slag per tapping, with a smaller amount of ferrochromium, ranging from 8.5 to 42 lb. It was ex-



**Fig. 2 — Relation between C and Si content of ferrochromium produced with C:Cr ratio of 0.87 to 1.17 in charge.**



Table V. Analyses of Products of Heats 38 and 41

	Analysis, Pct			
	Cr	Fe	Si	C
Heat 38:				
Primary metal	44.9	36.0	3.95	6.79
Metal after concentrate additions	41.9	49.6	0.19	5.25
Heat 41:				
Primary metal	50.8	38.7	0.46	7.91
Metal after concentrate additions	46.1	47.0	0.08	4.98
Metal after silicon addition	47.9	40.0	5.56	4.11
Primary slag	1.9	1.8	—	—
Slag after concentrate additions	15.0	2.2	—	—
Slag after silicon addition	5.3	2.0	—	—

pected that little metal would be tapped until the hearth was full of metal below the tap-hole level. Slag tapping temperatures were uniform at about 1570° C. When it was attempted to drain the furnace about 15 min after the third tapping, only a small quantity of slag and metal was obtained at the low tapping temperature of 1450° C. After the furnace had cooled, 296 lb of metal and 460 lb of slag were removed from the hearth.

Metal removed from the furnace in the first three tappings analyzed as follows, in pct:

Tap No.	Cr	Fe	Si	C	P
1	51.9	34.0	2.7	7.6	0.06
2	47.6	32.4	8.7	5.1	0.06
3	47.4	34.0	10.9	3.9	0.07

The slag averaged 2.9 pct Cr, and 1.8 pct Fe.

The most significant feature of this single continuous smelting test was the excellence of the dry-top smelting conditions. The slag tapping temperature at 1570° C should be an accurate measure of the actual smelting temperature of a charge of the composition used. Freezing of the melt on the hearth at the end of the test was likely the result of excessive chilling of the bath during tapping only a few minutes earlier. A

Table VI. Smelting Tests Made Under Acid Conditions.

Heat No.	57	61	62	63	64	65
Furnace						
Hearth	basic	acid	acid	acid	acid	acid
Charge, Lb.:						
Chromite Concentrate	60	100	80	80	81	81
Limestone	0	0	0	0	28.5	28.5
Quartz	13.5	22.5	18	18	23	23
Coal	0	58	46	37.5	51.5	51.5
Char	21	0	0	0	0	0
Charge Basicity	0.69	0.71	0.69	0.70	1.05	1.05
Charge, C:Cr Ratio	0.87:1	0.87:1	0.87:1	0.70:1	0.95:1	0.95:1
Metal:						
Analyses, Pct:						
Cr	48.8	46.5	46.8	48.2	48.6	46.6
Fe	35.9	33.1	31.7	33.5	31.8	33.1
Si	7.3	10.6	11.1	7.2	13.6	13.5
C	6.2	4.9	4.7	5.1	3.9	3.4
Recovery, Pct:						
Cr	84.2	91.8	86.2	86.2	91.1	94.8
Fe	75.6	77.7	77.5	75.9	80.5	89.9
Ratio Cr:Fe	1.36:1	1.40:1	1.48:1	1.44:1	1.53:1	1.40:1

somewhat higher smelting temperature may be desirable and should be attainable by reducing the proportion of quartz in the charge.

Although the test program is not far enough advanced to permit the drawing of definite conclusions, significant observations and tentative conclusions are as follows:

1—Single-stage batch smelting of Mouat concentrate, on a magnesite hearth and with a carbon:chromium ratio in the charge of 1.02:1, produced ferrochromium with a weighted average analysis for five tests of 49.1 pct Cr, 37.3 pct Fe, 4.0 pct Si, 6.5 pct C, less 0.01 pct S, and 0.10 P. Silicon content ranged from 1.03 to 7.89 pct, and carbon from 4.9 to 7.7 pct for individual tests. The average ratio of Cr:Fe in the metal was 1.32:1. Recoveries of chromium and iron in the metal averaged 96.5 and 94.1 pct, respectively.

2—The percentages of carbon and silicon in ferrochromium produced from charges having C:Cr ratios between 0.87 and 1.10:1 show a definite relationship to each other, which appears to have an important bearing on the smelting and refining of ferrochromium.

3—Selective reduction of iron from chromite in smelting on a basic hearth becomes pronounced when the C:Cr ratio of the charge is lowered to about 0.45:1.

4—Smelting on a silica hearth has promise of producing ferrochromium with a considerably higher Cr:Fe ratio than that of the chromite concentrate by preferential rejection of iron to the slag.

5—Silicon is much more readily oxidized from crude metal than is carbon. Hence, high-silicon, low-carbon crude metal should be aimed at for subsequent refining to low-carbon ferrochromium.

6—Continuous, open-top electric smelting of Mouat chromite concentrate appears feasible.

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# The Electrical Resistivity of Titanium Slags

by James L. Wyatt

The specific electrical resistivities of titanium-containing slags, with iron oxide contents ranging from 2 to 30 pct, are reported. Values of resistivity are shown as a function of the iron oxide content in the slags, and indicate that titanium slags are in general very low in specific electrical resistivity as compared with siliceous slags.

THE smelting of ilmenite to produce a slag rich in titanium, with pig-iron as a byproduct, introduces new concepts in electric smelting metallurgy. Titanium slags are characterized by low electrical resistance, thereby requiring a different type of electric furnace operation, and power supply sources substantially different from those encountered in normal steel melting and siliceous ore smelting furnaces. This paper describes special apparatus for determining specific electrical resistivity of titanium slags, and reports the values obtained on slags encountered in the process of smelting ilmenite ores. In an induction furnace under conditions approximating normal furnacing operation, 25 general heats and 6 special standardization and comparison heats were run. Results indicate relatively low resistivity. Resistivity depends primarily on slag composition, and, to a lesser degree, on temperature.

During the summer of 1947 a cooperative project between the National Lead Co. and the Bureau of Mines was conducted at Boulder City, Nevada, in the Electrometallurgical Laboratories of the Bureau.

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The project involved smelting of ilmenite ores in electric furnaces, and has been reported in detail.<sup>1</sup> The author participated as a member of the staff of the National Lead Co. during the entire campaign. One outstanding characteristic of the titaniferous slags, their apparently excellent and variable electrical conductivity, was considered sufficiently important to warrant further study.

Although little electric smelting of iron ores has been done in the United States, a certain amount of information is available for comparative purposes.

Personal experience in smelting siliceous iron ores in electric furnaces furnished further information for comparison. In general, silicate slags are relatively poor conductors of electricity. Current flow during smelting operations may be maintained through a floating layer of coke on top of the slag bath, or through a bath of molten iron beneath the slag. Silicate slags are not sufficiently conductive to furnish a path for current passage when normal furnace voltages are used.

Experimental smelting of a silicate iron ore was undertaken for comparative purposes. A fluid melt was not obtained until the FeO content was reduced to 15 pct. The resistivity increased as the FeO content decreased, FeO compounds being the most conductive of the various oxides in such a normal slag system. The converse appears to be true in slags containing large percentages of  $TiO_2$ . It has been found that titanium slags become molten with FeO percentages in excess of 30 pct, and that the conductivity becomes generally better as the FeO content of the slag diminishes. This phenomenon was demonstrated in the furnacing operations at Boulder City. During the initial smelting period furnace electrodes could be held immersed several inches in the slag, with tap selectors set for a no-load voltage of 70 v. As the FeO content decreased, the furnace electrodes would "walk up," until at one point in the process the tips would break the surface and arc on top of the slag. This was undesirable since direct arcing caused losses of important flux additions. The slag compositions under study at that time were such that losses due to surface arcing sometimes caused viscous slags to be formed. Forcing the electrodes into the slag bath by manual control to prevent surface arcing resulted in excessive power input and lack of control. Suitable low voltages were not available.

Measurement of the electrical resistivity of titanium slags at various operating temperatures and slag compositions was undertaken. It was believed that this information would be of use in the design of electric furnaces suitable for smelting ilmenite, with voltages, electrode sizes, and electrode spacing adapted specifically to titanium slags.



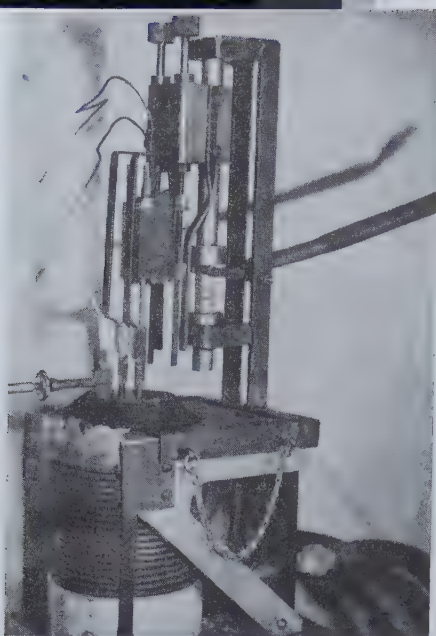


Fig. 1—Electrode control and support assembly.

A survey of pertinent literature revealed some enlightening information. Wejnarth,<sup>2</sup> prominent in the field of electrical conductivity, investigated iron-calcium and calcium meta-, ortho- and sesquisilicates. He noticed sharp breaks in conductivity at the point of primary crystallization, and concluded that monosilicates were the best conductors. High percentages of iron oxide gave high conductivity values; alumina additions to slags in equivalent proportions decreased the conductivity more than either lime or magnesia. In general, Wejnarth concluded that the dark-colored oxides of heavy metals were very good conductors, and that light-colored oxides of light metals were poor conductors.

Derge and Martin<sup>3</sup> measured the electrical conductivity of blast-furnace slags, in an attempt to demonstrate the occurrence of ionic conductivity. In the alumina-lime-silica system, using graphite electrodes and crucibles, they obtained the values given in table I.

Table I. Electrical Conductivity of Blast-Furnace Slags

Temp, °C	Resistivity, Ohm-cm
1,441	5.557
1,497	4.077
1,529	3.218
1,563	2.613
1,607	1.986

Thus an increase in temperature decreases the resistivity. Derge and Martin concluded that there was a certain amount of ionization, since an ionized fluid is characterized by this type of temperature-resistivity relationship.

Sauerwald and associates<sup>4</sup> experimented with electrolysis in the FeO-SiO<sub>2</sub> system, using an iron crucible and a concentric iron electrode. Very pure iron was plated out, substantiating the ionization theory of Derge and Martin.

Doelter<sup>5</sup> measured the electrical conductivity of molten silicates, principally hornblende, diopside, and augite. His experiments showed only an increase in conductivity with an increase in temperature.

Aiken,<sup>6</sup> Beckman,<sup>7</sup> Farup,<sup>8</sup> and others<sup>9-11</sup> conducted experiments in electrolysis and measured the electrical conductivity of various systems, but none used alternating current. Further, with the single exception of Martin, none of the researchers experimented at temperatures in excess of 1300°C. As far as the author knows, no one has ever attempted to measure the resistivity of a slag of varying composition and temperature, under conditions simulating those of electric smelting.

### Theoretical Considerations

In a molten system, the electrical impedance between two parallel electrode surfaces is directly proportional to the distance between them, and inversely proportional to the cross-sectional area of the electrode surface exposed. Stated in the form of an equation:

$$R = \frac{\rho L}{A} \quad [1]$$

Where  $R$  is the measured resistance across the electrodes.

$L$  is the distance between the electrode faces.

$A$  is the area of the electrode face.

$\rho$  is the specific resistance of the molten system.

Hence, to measure the specific resistance of a fluid, it is necessary to measure the distance between electrode surfaces, the electrode area, and the circuit impedance. Under experimental conditions of having graphite electrodes immersed in a molten bath of reducible oxides at 1500°C, direct measurement of electrical resistivity is extremely difficult. Electrode consumption and warpage are two of many factors that tend to complicate measurements under such circumstances.

It sometimes happens that the difference between the absolute values of two quantities may be accurately measured even though the absolute value of the individual quantities themselves cannot be determined. In the present work, a bath resistance was measured with electrodes immersed a known depth; then, by immediately lowering the electrodes to a different depth, the bath resistance was measured once more. Under these conditions,

$$R_1 = \frac{\rho L}{A_1} \text{ and } R_2 = \frac{\rho L}{A_2} \quad [2, 3]$$

Subtracting eq 3 from eq 2,

$$R_1 - R_2 = \Delta R = \frac{\rho L}{A_1} - \frac{\rho L}{A_2} \quad [4]$$

Solving for  $\rho$ ;

$$\rho = \frac{A_1 A_2 \Delta R}{L(A_2 - A_1)} \quad [5]$$

Thus  $\rho$ , the specific resistance, could be determined by immersing the electrodes to two different, known depths, determining the difference in total circuit impedance, measuring the respective areas of the exposed electrode surfaces, and substituting in eq 5.

### Experimental Equipment

Cylindrical graphite rods ½ in. in diameter and 12 in. long were selected as electrodes. Random measurements showed that the electrode diameters as received varied as much as 0.025 in., which could have introduced an error of up to 5 pct in resistivity



data. In order to assure uniformity in electrode dimensions, the lower 2 in. of each electrode were milled to produce a section 0.355 in. square. These dimensions were found to be accurate to within 0.001 in. on all electrodes.

A dual-purpose electrode assembly was designed and fabricated which allowed both individual adjustment and simultaneous movement of the electrodes in a vertical plane. Individual electrodes were actuated by means of a knurled hand screw feed. A maximum vertical movement of approximately 6 in. was possible.

A pivoted fork on a sliding shaft arrangement permitted vertical movement of the electrode assembly through definite predetermined distances. Suitable stops were provided to insure accurate positioning. Fig. 1 illustrates the apparatus in position on the induction furnace.

Electric Bridge Circuit

The electrical bridge circuit was patterned after the usual type of Wheatstone bridge, with a few minor exceptions. Alternating current was chosen in order to minimize complications caused by ionization of the slag. An oscillator whose frequency could be selected within the range of 0 to 30,000 cycles per second was selected as a current supply. A power transformer with an impedance of approximately 1000 ohms was added to the power circuit. It was required because the oscillator was designed to power a circuit with internal resistance of the order of 1000 ohms.

Little was known about the resistance of the slag, except that it was lower than that of silicate slags. Since values have been reported for siliceous slags ranging as low as one ohm, it was assumed that the titanium slag would be some fraction of one ohm. The two electrodes, together with connecting wire and clamps, had a circuit impedance of slightly less than one ohm. A total impedance of one ohm for each side of the bridge circuit was, therefore, chosen as an approximation.

Maximum sensitivity of a bridge circuit, as given by Hague,<sup>12</sup> is obtained when all arms of the bridge circuit are equal. Therefore, a standard one-ohm resistor was chosen as the arm of the bridge balancing the electrode circuit. The other two arms were formed by a variable rheostat-type resistance unit of approximately two ohms total impedance. This variable rheostat was calibrated from 0 to 1 in steps of 0.0005 units and could be interpolated to the nearest 0.0001 unit. A point contactor was used to divide the rheostat into two circuits. The bridge circuit was balanced by adjusting the contactor until minimum current flowed across the bridge. The reading of the rheostat at the balance point constituted the third arm of the bridge. The fourth arm was determined by subtracting the value of this reading from unity. For example, if the bridge balanced at a reading of 0.5462, then arm four would be 1.0000 — 0.5462, or 0.4538. To determine the impedance more accurately, readings of the cross-bridge current were taken on either side of the true balance point. An average of the two resulting values was considered the best possible reading obtainable. The current indicator across the bridge was a vacuum-tube voltmeter.

A platinum—platinum-10 pct rhodium thermocouple was selected to indicate temperature. The final thermocouple arrangement consisted of: (1) an outside protector tube formed by drilling out a

1/2 in. graphite rod, (2) a thin-wall Amersil closed-end tube to prevent carbon contamination, and (3) a thermocouple, surrounded by standard spacers. This arrangement appeared to be sufficiently sensitive to temperature changes to allow an accurate measurement at the instant the resistance measurements were taken.

Resistivity measurements were made during simulated smelting operations. The charge materials used for these tests were taken from those used at Boulder City, and identical slag compositions were used. Analyses of the components are shown in table II.

Table II. Analyses of Components of Charge Materials

Ore		Dolomite		Limestone		Coke	
Comp.	Pct	Comp.	Pct	Comp.	Pct	Comp.	Pct
TiO <sub>2</sub>	38.70	MgO	19.3	MgO	1.6	Fixed C	81.5
FeO	28.20	CaO	29.8	CaO	53.1	Volatile	11.4
Fe <sub>2</sub> O <sub>3</sub>	19.90	SiO <sub>2</sub>	2.3	SiO <sub>2</sub>	0.8	Ash	4.1
CaO	0.47	R <sub>2</sub> O <sub>3</sub>	2.0	R <sub>2</sub> O <sub>3</sub>	0.8	H <sub>2</sub> O	1.2
MgO	4.00	CO <sub>2</sub>	44.6	CO <sub>2</sub>	43.5	S	1.9
SiO <sub>2</sub>	4.10	H <sub>2</sub> O	0.4	H <sub>2</sub> O	0.2		
Al <sub>2</sub> O <sub>3</sub>	2.43						
Other	2.20						

Table III. Analyses of Charge and Resulting Slag

Charge		Slag Constituents		Glass Constituents		Slag Phases	
Comp.	Pct	Comp.	Pct	Comp.	Pct	Comp.	Pct
Ore	100.0	Glass	16.8	Al <sub>2</sub> O <sub>3</sub>	26.2	(Fe,Mg)O·2 TiO <sub>2</sub> + TiO <sub>2</sub>	67.6
Limestone	11.1	MgO	7.5	CaO	30.3	CaO·TiO <sub>2</sub>	15.6
Dolomite	0.88	CaO	6.5	SiO <sub>2</sub>	43.5	Glass	16.8
Coke	12.4	TiO <sub>2</sub>	67.3				
		FeO	1.9				
		Total	100.0	Total	100.0		

Table III shows the charge and resulting slag. The glass phases proposed for table III are anorthite, wollastonite, and gehlenite. The composition of the glassy phase is not known exactly, because it did not crystallize into phases.

Experimental Procedure

The general procedure was to weigh out suitable quantities of the component materials, mix them thoroughly and place most of the burden in the furnace crucible. The initial charge was melted as quickly as possible, the remainder of the burden charged, and the whole mass brought to liquid temperature. An initial pasty stage was encountered, followed by a melt of high fluidity having an FeO content in the range between 30 and 35 pct and a melting point of approximately 1300°C. Increasing the temperature beyond 1370°C resulted in vigorous boiling and frothing, and inability to maintain the melt in the crucible. Table IV gives the approximate temperature ranges for furnacing operations with various ranges of FeO content. The "Boiling Point" indicates the temperature of vigorous boiling and frothing referred to above.

Table IV also illustrates the relationship between the melting point and the FeO content of the slag. The figures represent recorded maximum and minimum temperatures taken from data sheets of all heats run. They serve to indicate that it was im-



practicable to obtain resistivity values for all compositions of slags at exactly the same temperature. Values reported, therefore, must consist of averaged results from many measurements at various temperatures.

Table IV. Temperature Ranges for Furnacing Operations

FeO Content, Pct	Melting Point, °C	"Boiling Point", °C
30-35	1,300	1,370
27-30	1,305	1,385
24-27	1,350	1,435
21-24	1,350	1,475
18-21	1,385	1,505
16-18	1,385	1,520
14-16	1,390	1,525
12-14	1,400	1,535
10-12	1,425	1,540
8-10	1,440	1,600
6- 8	1,450	1,600
4- 6	1,460	1,700
2- 4	1,460	1,700
0- 2		

To determine the resistance of the molten mass, it was necessary to turn off the furnace power supply. Thus, readings were taken as the temperature of the molten bath was decreasing. Successive sets of readings for each FeO content were taken, with an average temperature drop of 10° between readings.

The technique developed for obtaining a resistance reading consisted of the following steps: (1) Lowering each electrode separately until it contacted the molten slag surface. (2) Lowering the electrode assembly until the electrodes were immersed 1 in. in the molten slag. (3) Determining and recording (a) the temperature of the bath, (b) the reading of the variable rheostat at unit voltages on either side of the balance point of the bridge, and (c) the FeO content of the slag, by sampling and analyzing the slag later. (4) Raising the electrode assembly to the limit of an inserted stop, leaving the electrodes immersed in the slag ½ in. (5) Repeating the resistance and temperature measurements, and recording the results. (6) Duplicating the above procedure, obtaining a second set of readings as a check. (7) Removing the electrodes from the molten mass by raising the electrode assembly. (8) Turning the furnace on, and allowing the charge to continue smelting until the next set of readings was taken.

Resistivity Readings

An average of 12 sets of readings was taken during each heat. Using the technique outlined, 24 heats were run. A plot of the resulting resistivity values is shown in fig. 2. In this graph the resistivity is shown as a function of FeO, with average temperatures indicated at various points along the curve. The spread of the graph represents partly temperature effects and partly the results of FeO content changes during the intervals between successive resistivity measurements.

According to Derge and Martin, temperature has a profound effect on the specific resistivity of molten silicate slags. In order to determine the effect of temperature on titanium slags, one heat was run in which resistivity readings were taken as rapidly as possible over the complete temperature range for various FeO contents. A sample of slag was taken at the beginning and at the end of each series to

ascertain the percentage change in FeO content during the period the readings were taken. It was found that the change varied from as little as 0.1 pct to as much as 1 pct. The least change occurred during the measurements in the FeO range of 25 to 30 pct, while the greatest differential recorded was in the lowest range, namely, 2 to 10 pct FeO. This is natural, since the rate of reduction of FeO by carbon increases percentagewise as the heat progresses. The increased temperature required to keep the bath molten with decreasing FeO content also tends to accelerate the reduction process.

For purposes of comparison two groups of measured values have been selected. They are shown in table V. One group represents minimum variance of resistivity readings, while the other represents maximum variance. It should be noted that the minimum variance group is in the relatively high FeO percentage range, with only moderate FeO content change over the period during which the readings were taken. Conversely, the maximum deviation group is found in the lower FeO percentage

Table V. Resistance of Titania Slags as a Function of Temperature

Minimum Deviation			Maximum Deviation		
FeO, Pct	Temp, °C	Resistance	FeO, Pct	Temp, °C	Resistance
20.32	1,458	0.799	10.46	1,498	0.823
	1,450	0.798		1,484	0.824
	1,437	0.799		1,475	0.826
	1,423	0.792		1,471	0.833
	1,418	0.794		1,458	0.842
	1,416	0.797		1,448	0.854
	1,411	0.799		1,440	0.865
	1,408	0.798		1,432	0.862
	1,405	0.798		1,420	0.859
	1,403	0.796		1,408	0.858
19.89	1,399	0.798			

range, with a relatively high FeO content change during the period in which the readings were taken. Further cognizance should be taken of the temperature range; the range in temperature of the mini-

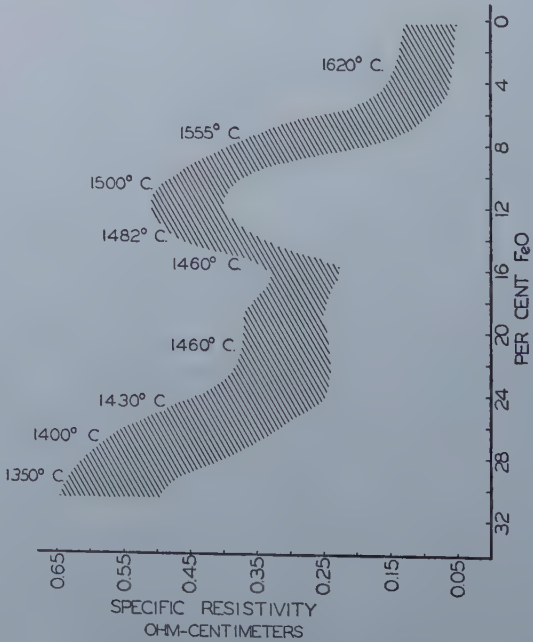


Fig. 2—Specific resistivity of titanium slags as a function of FeO content.



imum variance series is 59°, while that for the maximum variance series is 90°.

These two series represent maximum and minimum variance in resistivity readings caused by temperature phenomena. All other groups lay within these limits. The results of these figures indicate that temperature has little effect on the resistivity of titanium slags under normal smelting conditions in an electric furnace. More specifically, it can be stated that no more than 5 pct change in resistivity will be encountered for 100° change in temperature. In view of this conclusion, it is permissible, within reasonable limits, to consider the figures for the slag resistivity as though all measurements had been taken at the same temperature.

### Variable Factors

It was necessary to evaluate several variable factors in order to arrive at the most accurate resistivity values. The major variable was caused by exposure of graphite electrodes to an oxidizing atmosphere, as well as an oxidizing bath, for long

periods of time. In eq 5,  $\rho = \frac{A_1 A_2 \Delta R}{L(A_2 - A_1)}$ , a change

in area of 10 pct causes a change in the value of approximately 10 pct. During the series of heats, electrodes were collected at various stages of oxidation, and the change in area recorded. The change in area of the critical zone, that is, the lower 1 in., was plotted vs. the corresponding time of exposure; it was found that the degree of oxidation was a function of time, and that all points plotted lay on a smooth curve. A variable,  $K$ , was determined which took into account the effect of oxidation on the electrode surface areas, and on the distance between electrode surfaces. Values of  $K$  were plotted as a function of time. Using  $K$ , eq 5 becomes

$$\rho = K \Delta R \quad [6]$$

$$\text{Where } K = \frac{A_1 A_2}{L(A_2 - A_1)}$$

Values of  $K$  varied from 1.65 to 1.42 over a period of from 0 to 90 min. Fig. 3 shows a graph of values of  $K$  vs. time. The resistivity values plotted in fig. 3 have been corrected for electrode oxidation through the use of this plot. This was possible because the smelting rate in all heats was very similar. Proper values of  $K$  were determined for each reading by checking the data sheets to see how long the electrodes had been in service at the time the reading was taken. From the graph of  $K$  vs. time, the value of  $K$  corresponding to electrode time in service was selected, and the resistivity value multiplied by it.

The other variable considered worthy of evaluation was fringing effect. In a flux field of a magnet, the flux density is concentrated directly between the poles; however, an appreciable quantity of the flux lines radiate in arcs from one pole to another. In like manner the slag volumes surrounding the electrodes, both side and bottom, were potential carriers of electrical current. It was considered desirable that the quantitative effect of this fringing be determined.

Sodium tungstate, a salt of known specific resistivity at temperatures up to 1200°C, was selected as a standard for comparison. Three heats using sodium tungstate were run with the same equipment and technique as were used on the slags. The values obtained were plotted with standard values, and it was found that the curves were of the same general shape, but displaced somewhat. The values

at any specific temperature were in the same ratio as the values at any other temperature on the curves. Several specific values from the two curves were selected and compared. A correction factor was thus obtained. It was found that resistivity values as measured in the apparatus were too high; multiplying these results by 0.933 corrected the values to conform with the standard. Values plotted in fig. 2 are also corrected for fringing effects.

The possibility of nonuniformity in slag composition should be considered. In the experimental operation, a slag depth of from 2 to 4 in. was obtained, the slag depth gradually decreasing as iron oxide was reduced from the melt. At the same time

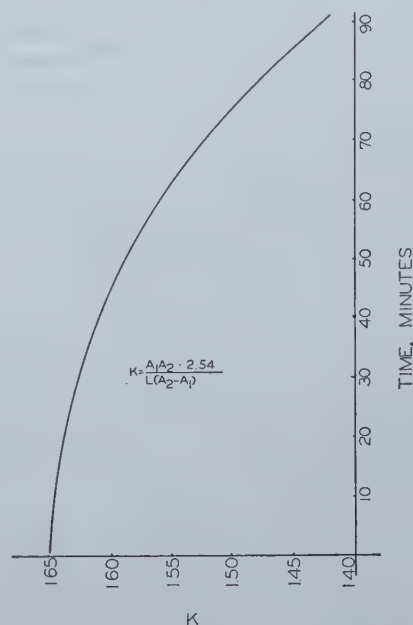


Fig. 3—Correction factor as a function of time.

an increasing depth of metallic iron was accumulated beneath the slag layer. The minimum slag depth, calculated from slag and metal volumes, was approximately 2 in. The electrodes were alternately immersed ½ and 1 in. into the slag, so that in the latter case a volume of slag was investigated which represented approximately half the total volume of slag in the crucible. If end and side fringing conductivity are considered, an even greater portion of the slag was under investigation with each measurement. Thus a lack of uniformity in the slag, if such existed after the vigorous mixing action of induction heating, could have been of little consequence. Previous investigators have used techniques of immersing electrodes only one-sixteenth inch below the surface of the melt.

It is felt that results reported indicate reasonably accurate resistivities for the bulk of the slag, though this may be open to some question. Measuring resistivities at a greater depth probably would have added serious errors because of the proximity of the electrodes to the molten metal beneath the slag.

Inasmuch as graphite electrodes were used, some reduction of FeO from the slag must have occurred at the slag-electrode interface. The slag immediately surrounding the electrodes thus may possibly have differed slightly from the bulk of the slag. Since a graphite crucible was used, and since finely dispersed carbon was prevalent in the slag as the reducing agent, no estimation of the effect on slag resistivity is attempted. Little is known about slag-



electrode interface reactions in respect to conductivity, the area being complicated by gaseous evolution, metal formation, heat requirements, and current densities. However, it would be suspected that the total impedance would be increased as a result of slag-electrode reactions, thus giving resistivities slightly higher than the true value. Alternating current was used to minimize ionic conduction. Evaluation of electrode surface resistance is not attempted.

One heat was run using a charge of siliceous iron ore for comparative purposes. No values of resistivity could be obtained for FeO contents above 9 pct because of the viscosity of the slag. Values actually measured are of dubious value because of lack of bridge sensitivity for high resistances, but between 4 and 9 pct FeO, the resistivity of the siliceous slags averaged 9 ohm-cm, and for FeO contents between 1 and 3 pct, resistivity values ranged between 1.2 and 1.8 ohm-cm. These values are in general agreement with the results published by Derge and Martin. On the basis of this meager information, it is proposed that titanium slags are in the order of 5 to 50 times as conductive as iron-bearing siliceous slags containing no titanium dioxide.

### Summary

The specific electrical resistivities of slags containing large percentages of titanium dioxide have been measured and reported. Results indicate that the electrical resistivity of molten titanium slag is not greatly affected by temperature, but is definitely a function of the FeO content.

The lack of temperature effect is noticeably different from reported results of most other investigators. The electrical resistivity of oxide systems decreases sharply with temperature increases, and in a uniform manner, such that plotting the log specific conductivity vs. reciprocal absolute temperature gives a straight line relationship. No such phenomenon was noted specifically in the titanium slags investigated. An explanation may be that the system was rather complex and of constantly changing composition. No correlation between resistivity data and phase changes was attempted, though a summary examination did indicate a relationship between drastic resistivity trends and phase changes in the solidified samples of slag.

Maximum resistivity values were found to lie in the ranges of 24 to 35 pct FeO and 8 to 12 pct FeO, with very sharp reduction in resistivity from 8 to 3 pct FeO. This agrees very well with actual experience in smelting ilmenite ores in pilot scale electric furnaces under similar conditions.

It has been established that compounds of titanium, a light metal which forms a white oxide, are the most conductive of the phases normally encountered in smelting operations involving compounds of iron, silicon, titanium, calcium, and magnesium. This is contrary to the general conclusions drawn by Wejnarth, who reported, on the basis of conductivity of slag systems, that light-colored oxides of light metals are poor conductors of electricity.

It has been shown that titanium slags have extremely low electrical resistivity in comparison to normal siliceous slags, on the basis of values reported by other authors and limited experimental work, to the extent of being up to 50 times as conductive. Because of this, it can be definitely stated

that electric furnaces for smelting titaniferous iron ores must be specially designed in order to accomplish satisfactory furnacing. Electrode spacing and minimum voltages must be so chosen as to allow immersion of electrodes in the slag bath at all times, without excessive power input. Herein are furnished sufficient data to allow the design of proper smelting installations should commercial smelting of ilmenite or other titanium-bearing materials be undertaken.

The apparatus developed for this project should prove useful for investigation of electrical properties of any fluid at any temperature, since the method used is not dependent on the material of which the electrodes are composed, and could be applied equally well to copper, platinum, or other kinds of electrodes.

Of primary importance, the results of this investigation explain why certain unsatisfactory operating characteristics were shown by the electric furnaces used for the smelting of ilmenite at the Bureau of Mines Station, Boulder City, Nevada.

### Acknowledgments

The author wishes to express his appreciation to the personnel of the Titanium Division of the National Lead Co. for the use of valuable basic experimental data, and to the management for granting permission to publish the paper. The kind assistance and helpful suggestions of faculty and staff of the University of Kentucky College of Engineering is gratefully acknowledged. The author is especially indebted to R. P. Smith, Chief Development Engineer of the Titanium Division of National Lead Co., for his continued personal interest, and for making arrangements to supply raw materials and special equipment necessary to the project.

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# The Intermittent Oxidation of Some Nickel-Chromium Base Alloys

by B. Lustman

IT has been known for a number of years that the addition of certain alkaline-earth and rare-earth metals to nickel-chromium base electric resistance alloys causes marked increase in their oxidation resistance as measured in an intermittent oxidation test similar to the ASTM—B 76-39 test. However, the mechanism whereby such additions confer protection is still unknown. On the basis of the experimental observation that the increase in life in intermittent tests of nickel-base alloys is proportional to the atomic radius of the added element, Hessenbruch<sup>1</sup> has proposed that the added metal ions occupy holes in the oxide lattice which prevent diffusion of nickel ions in the oxide. Horn<sup>2</sup> has postulated that the effect of such additions is to accelerate the rate of diffusion of chromium atoms in the metal and thus to favor the formation of  $\text{Cr}_2\text{O}_3$  scales. Hickman and Gulbransen<sup>3</sup> concluded from electron diffraction observation that the addition of the elements in question results in the formation of a barrier to the diffusion of nickel ions to the surface.

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In connection with some experiments conducted to develop a test for the resistance to oxidation of alloys in massive form under conditions of intermittent heating and cooling, some features of the oxidation of nickel-chromium base alloys were revealed which may serve to elucidate the mechanism of protection conferred by rare-earth and alkaline-earth elements. Specimens of cylindrical shape 0.360 in. diam x 0.37 in. long were placed in alumina thimbles and inserted into and withdrawn from a Globar-heated furnace operating at 2150°F at 7.5-min intervals. The weight of oxygen absorbed as well as the weight of oxide spalled were measured at intervals. With the particular experimental conditions used, the specimens in a 7.5-min cycle were at temperature for 2 min which corresponds to the heating time of the ASTM test. The weight changes of similar specimens under conditions of continuous heating in air at 2150°F were also measured. The specimens after oxidation were examined metal-

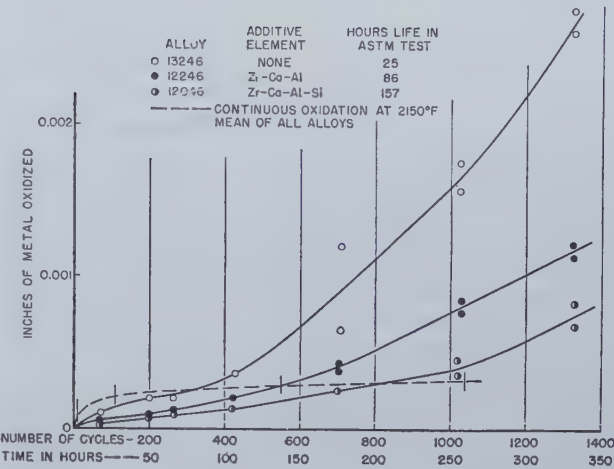


Fig. 1—Results of intermittent oxidation tests and continuous tests on bulk specimens at 2150°F.

lographically and samples of the spalled oxide collected for X-ray diffraction identification of the phases.

The specimens used were from the same lot of material used by Hickman and Gulbransen<sup>3</sup> and had the compositions shown in table I. Included in table I are results of ASTM life tests on the materials in the form of wires. These materials, their composition and the ASTM life test data thereon were all supplied by F. E. Bash of the Driver-Harris Co. It may be noted that alloy 13246 of 80 pct nickel, 20 pct chromium nominal composition showed the shortest life in the ASTM test; alloy 12246 with the addition of small amounts of the elements zirconium, calcium, and aluminum, intermediate life; and alloy 12046 with the further addition of silicon, the longest life.

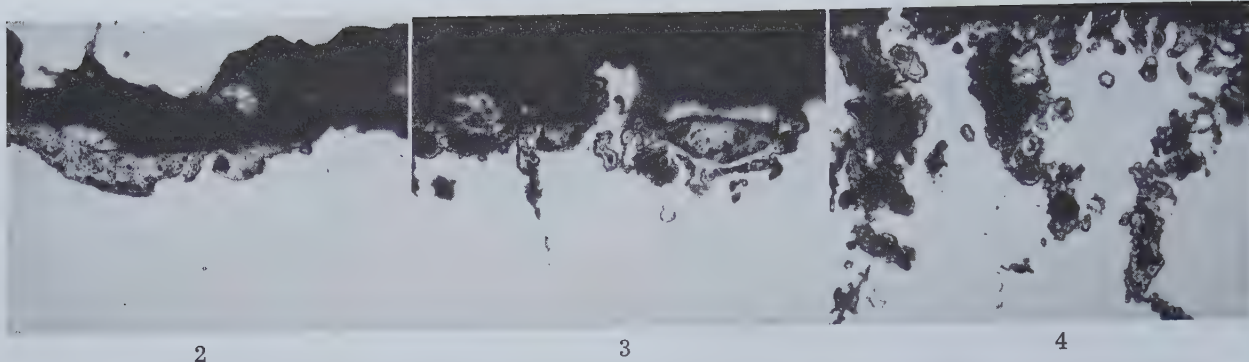
In fig. 1 are shown the results of intermittent oxidation tests made on bulk specimens at 2150°F as well as continuous tests conducted at the same temperature. Duplicate tests were made on each specimen. The ordinate scale, inches of metal oxidized, was derived from the experimentally observed weight gain of oxygen by assuming the scale to be entirely  $\text{Cr}_2\text{O}_3$ . It may be noted that the metal-loss curves during intermittent oxidation show a constant or continuously increasing rate of weight

Table I. Analysis of Samples

Heat No.	C	Mn	Si	Cr	Ni	Fe	Zr	Ca	Al	Mg	Useful* Life at 2150°F
12046	0.08	0.01	1.39	19.91	Bal.	0.34	0.10	0.024	0.07		157
12246	0.08	0.01	0.30	19.98	Bal.	0.32	0.05	0.029	0.08		86
13246	0.12	1.70	0.30	19.98	Bal.	0.20				0.006	25

\* The "useful life" is the time in hours required for a 10 pct increase in resistance in the ASTM test B 76-39.





Figs. 2-4—Oxidized 1529 cycles at 2150°F.

Fig. 2. Sample 13246. Fig. 3. Sample 12246. Fig. 4. Sample 12046. The gray portions are oxide, the white portions are metal. Unetched. X750. Area reduced approximately three quarters in reproduction.

gain of oxygen (or thickness of metal oxidized) with time or cycles of oxidation. Likewise, there is a direct correlation between life measured in the ASTM test and thickness of metal oxidized during the intermittent test. On continuous oxidation, on the other hand, the rate of metal loss by oxidation decreases continuously with time and furthermore, the oxidation curves of each of the three alloys are practically identical within the limits of experimental error. Such differences as could be noted during continuous oxidation indicated greater metal loss for the alloy which showed least loss on intermittent oxidation.

X-ray diffraction results on both the spalled and adhering oxide present on each alloy after oxidation showed, similar to the electron diffraction findings of Hickman and Gulbransen on these same alloys, that  $\text{Cr}_2\text{O}_3$  was the principal constituent of the scale in the case of the alloy 12046 showing longest ASTM life and least weight loss in the intermittent test, and that admixtures of  $\text{NiO}$ ,  $\text{Cr}_2\text{O}_3$ , and spinel were present in the other alloys.\*

\* X-ray measurements were made by S. Beatty of the Westinghouse Research Laboratories.

The microstructures of the alloys after oxidation are quite instructive in indicating the possible cause for the considerable difference in behavior between intermittent and continuous oxidation as well as the mechanism of protection by the addition of the alkaline-earth metals and silicon to the base composition. In Figs. 2, 3, and 4 are shown the surfaces of the oxidized alloys 13246, 12246, and 12046 respectively after 1529 cycles of oxidation at 2150°F. It may be noted that the oxide-metal interface is quite smooth in case of alloy 13246 which showed most oxidation in the intermittent test and shortest life in the ASTM test; in case of alloy 12246, containing Zr, Ca, and Al, whose oxidation rate in the intermittent test and life in the ASTM test were intermediate, there was appreciable internal penetration of the oxide; while alloy 12046 containing Si as well as Zr, Ca, and Al, showed considerable internal penetration of oxide, least oxidation in the intermittent test and longest ASTM life. A similar trend of internal penetration of oxide was found in case of continuous oxidation. It was likewise found that the amount of oxide spalled during the intermittent test relative to the total weight of oxide formed increased with increasing weight loss or decreasing depth of internal oxidation. Results similar to those found here have also been noted in alloys of base composition 61.5 pct Ni, 16.5 pct Cr, 22 pct Fe.

At the oxide-metal interface, oxygen diffuses from

the oxide into the base metal and metal ions pass from the metal into the oxide. If the latter process is relatively rapid compared to the former, the movement of the interface into the metal will be sufficiently rapid to prevent marked internal oxidation. If, however, following the reasoning of Hessenbruch and of Hickman and Gulbransen, it is assumed that the addition of rare-earth or alkaline-earth elements causes the formation of a barrier which prevents ready passage of metal ions into or through the oxide, oxygen will penetrate the base metal to a much greater depth resulting in more internal oxidation the more restricted the outward diffusion of metal ions. The presence of such an internal oxide will tend to key the oxide to the metal resulting in less spalling on intermittent heating and cooling and correspondingly less oxidation of metal. During continuous oxidation, on the other hand, where spalling of the oxide, because of differential contraction on cooling, is not a factor, internal oxidation will not greatly affect the overall rate of oxidation.

The assumption of the formation of a barrier by the addition of certain elements serves also to explain the composition of the scale. If metal ions can pass freely into the oxide scale, the gross composition of the latter will tend to approach the base metal composition and to consist of  $\text{NiO}$ , spinels, and  $\text{Cr}_2\text{O}_3$ . If, however, the passage of metal ions into the oxide phase is restricted by some barrier, the diffusion of oxygen into the base metal will predominate; the inwardly diffusing oxygen will react to precipitate the oxide phase most stable in contact with metal of the composition here used (i.e.,  $\text{Cr}_2\text{O}_3$ ), and on continued oxidation this phase will be incorporated into the external oxide. Thus alloys showing pronounced internal oxidation may be expected to exhibit scales consisting predominately of  $\text{Cr}_2\text{O}_3$ .

It thus appears that improvement of the oxidation behavior in intermittent tests of nickel-chromium and iron-nickel-chromium base alloys by the addition of small amounts of certain elements is achieved by the tendency of these elements to promote internal oxidation and thus to prevent spalling of the protective oxide scale during cycles of heating and cooling.

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# Austenite Formation During Tempering and Its Effects on Mechanical Properties

by E. F. Bailey and W. J. Harris, Jr.

Austenite may be formed during tempering below  $A_1$  as determined in continuous heating. The amount formed and the decomposition characteristics depend on time and temperature of tempering. Transformation of this austenite during cooling or by plastic deformation in tensile or impact testing results in increased tensile strength, decreased ductility, and reduced notch toughness.

THE temperature of the ferrite to austenite reaction is established frequently by continuous heating experiments. However, equilibrium studies of this reaction have demonstrated that austenite may form at temperatures considerably below those at which the reaction is first observed during continuous heating. Because of this discrepancy, tempering is sometimes performed above the true critical temperature and in these cases austenite forms during tempering. The lowest temperature at which austenite forms and the kinetics of the reaction have been studied by Bain,<sup>1</sup> Bleakney and Grosvenor,<sup>2</sup> and Dube and Cunningham.<sup>3</sup> This austenite can affect the properties either as austenite *per se*, if it is retained at room temperature, or as a decomposition product if it transforms.

The effect of austenite formation during tempering on low temperature impact properties of an 8½ pct nickel steel was reported by Brophy and Miller<sup>4</sup> in work published after the present investigation was initiated. They concluded that the improvement in low-temperature notch toughness which followed tempering at certain temperatures could be attributed to the austenite formed during tempering.

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Kramer et al.<sup>5</sup> found anomalous hardness increases and embrittlement after tempering of a low-carbon manganese-nickel steel. They concluded that austenite formed during tempering, and that the decomposition products were responsible for the increase in hardness and the embrittlement. Quantitative correlations of the microconstituents and mechanical properties were not made by these investigators.

The present study was undertaken in order to establish the kinetics of formation of austenite at various temperatures, the characteristics of the decomposition of this austenite, and the relationship between mechanical properties and the phases present.

## Experimental Procedure

A low-carbon manganese-nickel steel was selected because of the sluggishness of its austenite decomposition reactions. The composition of this steel in percent was: C, 0.10; Mn, 3.52; Ni, 2.34; Mo, 0.52; Cr, 0.17; Si, 0.19; V, 0.15; P, 0.019; and S, 0.020. Samples were prepared by forging sections from a large ingot to ¾ in. bars.

Formation and decomposition of austenite were investigated by dilatometric techniques which were checked by X-ray measurements. Dilatometer specimens were hollow cylinders 1 in. long, ½ in. diam, with a ⅛ in. central hole. All specimens were austenitized for 1 hr at 1650°F and quenched in water prior to insertion in the dilatometer. Oxidation was prevented by using an inert atmosphere of purified nitrogen. Dilation was measured with a dial gauge which could be read by interpolation to 0.00005 in. Temperature was maintained within  $\pm 3^\circ\text{F}$  by a Brown Electronik Controller. Chromel-alumel thermocouple leads were welded to opposite ends of the specimen with the specimen serving as the hot junction. As a check on temperature uniformity comparison was made of the specimen temperature as measured with the chromel-alumel leads and the temperature of the center of the specimen as measured with a calibrated platinum-platinum-rhodium thermocouple embedded in asbestos in the central hole of the specimen. During heating a 5°F temperature difference was noted below 1000°F, but none above, while in cooling, a 5°F difference was observed from 1300° to 735°F, but none below. Heating rates of 35°F per min and cooling rates of 60°F per min were employed for all dilatometric studies. For transformation studies below room temperature, the dilatometer was allowed to cool to 150°F and then was quenched into liquid nitrogen.



At any temperature the fraction of specimen transformed to austenite was considered to be equal to the contraction during holding divided by the distance between the 100 pct ferrite and 100 pct austenite dilation lines at that temperature. When necessary these distances were measured between extrapolated dilation lines. The fraction transformed to martensite at a given temperature was calculated according to the method of Fletcher and Cohen.<sup>6</sup>

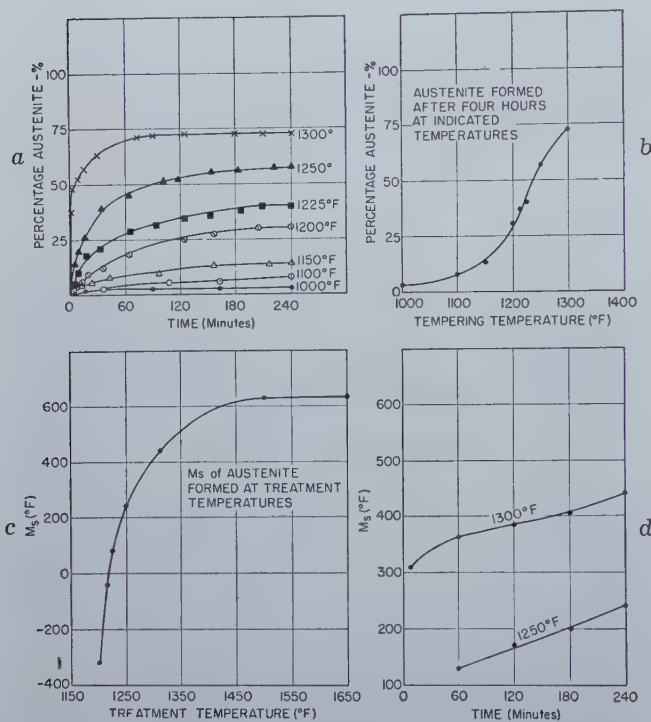
In order to establish the accuracy of the dilatometer, the amount of austenite retained at room temperature was calculated for specimens held at a series of temperatures and cooled in the dilatometer. X-ray determinations of the amount of retained austenite were made at the Massachusetts Institute

**Table I. Austenite Content at Room Temperature, 1/2 in. Rounds**

Thermal Treatment	Austenite, Pct	
	X-ray	Dilatometer
1650° (1 hr)—water quenched	1*	
1650° (1 hr)—air cooled	2	
1650° (1 hr)—slow cooled	5.3	5.3†
1650° (1 hr)—+ 1100° (4 hr)	8.5*	8.0†

\* Water quenched after heat treatment.

† Cooled at a rate of 60° per min after heat treatment.



**Fig. 1—Transformation characteristics of austenite formed at indicated temperatures.**

a. Rate of austenite formation. b. Amount of austenite formed after 4 hr at temperature; c.  $M_s$  as a function of austenite forming temperature; d. Change in  $M_s$  with time at temperature.

of Technology by the precise method of Averbach and Cohen<sup>7</sup> using specimens of the same steel which were heat treated at the same temperatures, for the same time, but quenched in water. (At the time this check was made, it had been established that austenite formed at these temperatures did not transform during cooling.)

Results are given in table I. From the excellent agreement, it can be said that contractions at temperature can be attributed entirely to austenite formation in this steel.

High-temperature X-ray studies were made by L. S. Birks in a high-temperature Geiger counter unit designed by him.<sup>8</sup> Formation and decomposition of austenite were observed in the same temperature range as were found by use of the dilatometer.

All mechanical property specimens were first austenitized 4 hr at 1650°F and then cooled at a rate

of 60°F per min (from 1300° to 300°F). Then they were given thermal cycles identical with dilatometer specimens in order to produce known amounts of austenite. Tempering treatments of 4 hr at temperatures of 1100°, 1200°, 1225°, 1250°, and 1300°F were used. It is recognized that tempering is defined as treatment below  $A_{c1}$ . However, for purposes of this study, tempering is used to indicate a reheating after quenching.

Duplicate tensile tests for each treatment were made at room temperature. Simultaneous readings of diameter and load were made in order to calculate true stress and true strain. The specimens were standard 0.505-in. bars with a 2-in. gauge length.

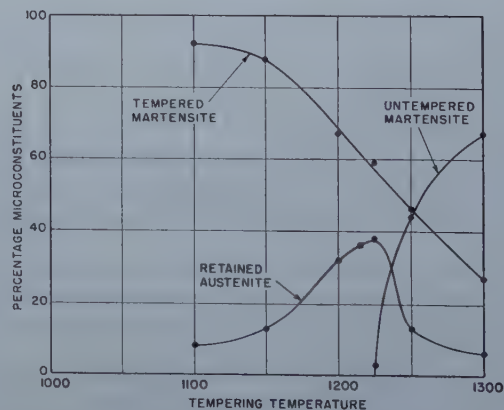
From 10 to 40 standard Charpy V-notch specimens were broken in a 240 ft-lb machine at a series of temperatures covering the range from ductile to brittle behavior.

Metallographic techniques for measurement or identification of austenite were unsuccessful for the low-carbon martensite did not temper to a dark phase distinguishable from austenite.  $M_s$  determinations utilizing the Greninger-Troiano method could, therefore, not be made.

Grain size measurements were possible in fully martensitic specimens and they were made by examination of several fields at X100 with a Grossman eyepiece. Grain size of specimens which were mixtures of austenite and martensite could not be established because of the complexities of the microstructure.

## Results, Transformation Characteristics

Dilatometric studies indicated that austenite began to form in this steel at 1220°F during continuous heating at a rate of 35°F per min. However, when



**Fig. 2—Percentage microconstituents at room temperature after tempering for 4 hr.**

Temperature is in degrees F.



heating was stopped at 1000°F and the specimen held at temperature for 4 hr, about 3 pct of austenite appeared to form. Therefore, the true  $A_1$  is below 1000°F in this steel.

As the temperature was raised above 1000°F, the initial rate of austenite formation increased as shown in fig. 1a. The amount of austenite formed after holding for 4 hr likewise increased (fig. 1b). These figures indicate that the initial rate of austenite formation and the amount formed in 4 hr started to increase rapidly at about 1200°F.

Decomposition of the austenite during cooling occurred in a martensite-like reaction. Kramer<sup>5</sup> has shown that the temperature of the beginning of

effect can be explained either by a change in composition or of grain size of the austenite. It is considered unlikely that the composition could change without a related change in quantity. In order to check the possibility of its being a grain size effect,  $M_s$  was determined for specimens with two different grain sizes cooled from 1650°F. An ASTM grain size of 9 gave an  $M_s$  of 630°F and a grain size of 6, an  $M_s$  of 720°F. It appears, therefore, that grain growth of austenite during holding may account for the increases of  $M_s$ .

Study of austenite formation and decomposition showed that since  $M_s$  was at room temperature for specimens treated at 1220°F, those treated below contained tempered martensite and austenite while those treated above contained tempered martensite, untempered martensite, and retained austenite. The amount of tempered martensite was equal to the difference between 100 pct and the amount of austenite formed during tempering. The quantity of martensite formed between  $M_s$  and room temperature was calculated from the expansions which occurred during transformation.<sup>6</sup> The amount of retained austenite was the difference between the amount of austenite formed and that decomposed. Fig. 2 shows the amounts of the various structures in relation to the tempering temperature.

Mechanical Properties, Tensile Results

Results of tensile tests as a function of tempering temperature are shown in fig. 3.\* The structures present and the amounts of retained austenite are indicated also. The effect of retained austenite on tensile properties probably depends on whether or not it is transformed by plastic deformation. Several

\* The drop in elongation at 1100°F was accompanied by longitudinal cracking of the tensile bars.

yieldings observed in specimens tempered from 1150° to 1225°F were attributed to such a transformation which was considered to account for increases in elongation, reduction of area, and tensile strength. Since only small amounts of austenite were present in specimens treated at other temperatures and the extent of transformation of this austenite could not be determined, the effect of austenite *per se* could not be established.

Since retained austenite does not transform by elastic deformation, an attempt was made to determine the effect of each constituent on yield strength by using the percentages given in fig. 2, an experimental yield strength of untempered martensite given in fig. 4, and estimated yield strengths for tempered martensite and austenite also given in

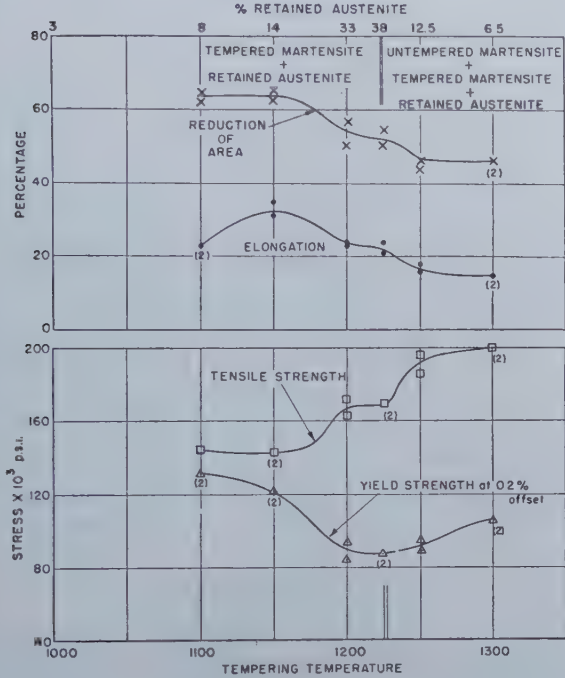


Fig. 3—Tensile properties. Temperature is in degrees F.

transformation of steels, similar to the one used in this study, is constant for a wide range of cooling rates. In the present study, no isothermal decomposition was detected upon holding up to 4 hr at 700° and 600°F.

Fig. 1c shows the relations between the temperature of austenite formation and the  $M_s$  of the austenite formed. Austenite formed below 1200°F had an  $M_s$  below -320°F, that formed at 1220°, an  $M_s$  of room temperature, and as the temperature was raised from 1220° to 1450°F,  $M_s$  increased to 630°F.

Study of the iron-carbon-manganese phase diagram<sup>9</sup> reveals the existence of a boundary between a three-phase field and a two-phase field at 1200°F for an alloy with equivalent composition of the steel under study considering 1 pct of nickel to have the effect of ½ pct of manganese. Differences in transformation kinetics between treatments below 1200°F and those above can be accounted for by the existence of this boundary with the very low  $M_s$  for austenite formed below 1200°F being due to a high concentration of carbon and alloying elements in the austenite in the three-phase region.

An increase in holding time at a given temperature raised  $M_s$  even after the rate of austenite formation was very slow (figs. 1a and 1d). This

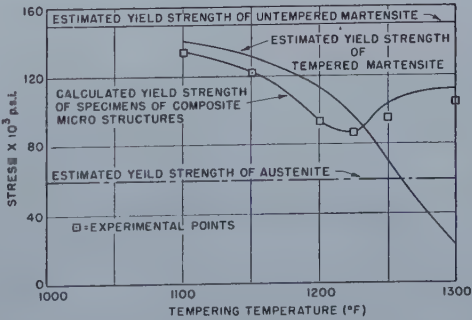


Fig. 4—Effect of microconstituents on the yield strength at 0.2 pct offset.



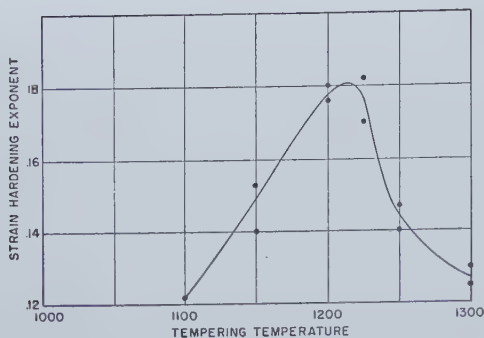


Fig. 5—Strain hardening exponent as a function of tempering temperature. Temperature is in degrees F.

fig. 4. The estimated values were selected after study of the properties of austenite<sup>21</sup> and of tempered, low-carbon steels. The yield-strength curve given in fig. 4 was obtained by multiplying the percentage present by the yield strength for each structure on the assumption that each phase contributes in proportion to the amount present. As can be seen, the experimental and the calculated yield strengths are in good agreement, and the assumption appears to be approximately correct.

The strain hardening exponent (taken from the plot of log true stress vs. log true strain) when plotted as a function of the tempering temperature, fig. 5, shows that as the amount of austenite increases the exponent increases and that specimens with similar austenite contents have similar exponents.

Results of the impact tests are shown in fig. 6. When untempered martensite (1250°, 1300°F†) or partially tempered martensite (1100°F) are present, transition temperature is high and maximum energy low. In the absence of untempered martensite, more complete tempering raises maximum energy and lowers transition temperature† (1150°, 1200°F).

† Tempering temperatures.

‡ Transition temperature refers to the temperature range in which the energy absorbed in impact tests changes from a high to a low value.

Transition temperature is increased when large amounts of retained austenite are present, despite

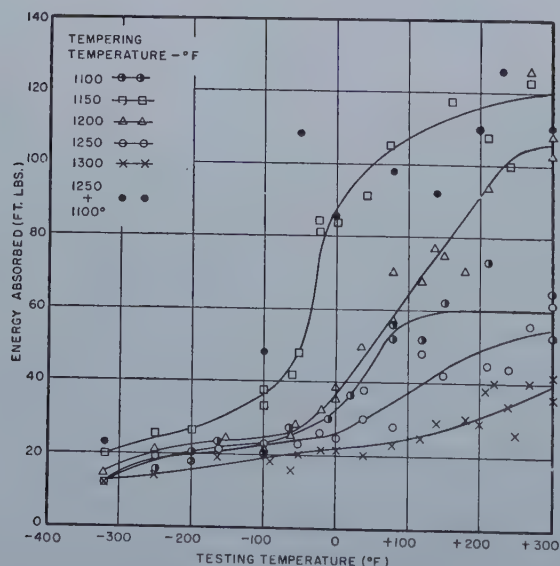


Fig. 6—Impact energy vs. testing temperature for material tempered at indicated temperatures.

the well tempered martensite (compare 1200° with 1150°F). This loss of notch toughness is attributed to retained austenite either because of the complexities of the microstructure or, more likely, because of transformation of the austenite during testing.

The embrittlement resulting from transformation of austenite to martensite during cooling can be eliminated by retempering.

## Summary and Conclusions

1. In a low-carbon manganese-nickel steel, austenite appears to form at 1220°F during heating at 35° per min. However, upon prolonged heating between 1000° and 1220°F, up to 38 pct of austenite may be formed. This austenite coexists with tempered martensite.

2. Upon tempering above 1220°F, the austenite which forms may transform partially to martensite during cooling, and give rise to mixtures of retained austenite and tempered and untempered martensite at room temperature.

3. The austenite formed during tempering and retained after cooling to room temperature lowers yield strength. Large amounts of retained austenite increase tensile strength, reduce elongation and reduction of area, and raise transition temperature in the Charpy V-notch impact test. These latter effects are attributed to decomposition of the austenite by plastic deformation during the test.

4. Martensite formed from decomposition of the austenite during cooling from the tempering temperature increases tensile strength, reduces elongation and reduction of area, and lowers notch toughness. Embrittlement caused by this martensite may be eliminated by retempering.

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The authors wish to express their gratitude for the interest of O. T. Marzke. The cooperation of Stewart Toleman and I. R. Kramer who developed this alloy of high hardenability is acknowledged. The quantitative measurements of retained austenite performed by B. L. Averbach at M.I.T. and the willingness of L. S. Birks to apply his high-temperature X-ray equipment are gratefully appreciated.

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# Recrystallization Reaction Kinetics and Texture Studies of a 50 Iron 50 Nickel Alloy

by William E. Seymour and David Harker

Recrystallization rate curves for a 50 iron 50 nickel alloy are plotted from data obtained using an X-ray spectrometer, and an activation energy is calculated for the reaction. A multiple crystal orientation is found for the as-rolled material, and the cube texture when recrystallized in the range of 500° to 600°C. It is well established that the directions of easiest magnetization in a single crystal of alpha iron are of the form  $\langle 100 \rangle$ , while for nickel the corresponding directions are of the form  $\langle 111 \rangle$ . However, when iron is added to nickel the  $\langle 111 \rangle$  directions persist as the easiest for magnetization until about 25 pct iron has been reached. In alloys containing more than 25 pct iron the directions of easiest magnetization change from  $\langle 111 \rangle$  to  $\langle 100 \rangle$ .<sup>1</sup>

CERTAIN alloys of iron and nickel, when rolled and annealed, possess a preferred crystal orientation: (001) in the rolling plane and [100] in the rolling direction, when recrystallized at 850° to 1050°C after approximately 98 pct cold reduction. Since the preferred orientation makes a direction of easiest magnetization coincide with the rolling direction, these alloys, especially a 50 pct iron in nickel alloy, have found wide application in the electrical industry<sup>2</sup> for choke coils and special types of transformers.

The rate of the recrystallization reaction was studied at temperatures ranging from 500° to 600°C. The heat of activation for the reaction was calculated from the observed rates, and crystal orientation determinations were made before and after recrystallization.

A vacuum melted iron-nickel alloy\* analyzing 49.6 pct nickel, 0.018 pct carbon, and 0.30 pct

\* The history of this heat is as follows: Hot forged at 1175°C to 1 x 3 in. x maximum length. Cut into 1 x 3 x 5½ in. pieces and ground on all four sides. Hot rolled at 1050°C to ¾ x 3 in. x maximum length. Annealed 1 hr at 1000°C in pure dry hydrogen. Cold rolled to 0.100 x 3 in. x maximum length. Annealed 5 hr in pure dry hydrogen at 700°C. Cold rolled to 0.014 x 3 in. x maximum length. Slit into 0.014 x ½ in. x maximum length strips and rolled on a Sendzimir mill to 0.002 x ½ in. x coil.

manganese was used for the experiments. The alloy was cold-rolled 98 pct into strips ½ in. wide by 0.002 in. thick. Specimens 1 in. long were sealed under a vacuum (approximately 10<sup>-8</sup> mm Hg) in ½ in. ID pyrex glass tubes. For heat treatment these tubes were fastened to Nicrohm wires and submerged in a molten salt bath controlled to ±2°C. (The maximum measurement error was within 3°C.) The time at temperature was varied logarithmically from one sample to another, and runs were made at 500°, 525°, 550° and 575°C. A molten lead bath was used for a run at 600°C which was controlled to the same accuracy.

To determine the extent of recrystallization after a particular time at a given temperature, a method was used suggested by the work of Decker, Asp, and Harker.<sup>3,4</sup> This method employs an X-ray spectrometer whereby X rays are diffracted from crystallites whose diffracting atom planes are parallel to the rolling plane of the specimen. The intensities of the diffracted rays are measured by a Geiger counter. The counter can be rotated through a range of angle, and can be motor driven through this range at a speed of 2° per min. The measured intensities are plotted vs. angle by a potentiometer recorder.

In a 50 pct iron-nickel alloy it was found that only (200) reflections were obtained from the rolling plane with recrystallized material, and that only (220) reflections were obtained from the rolling plane with unrecrystallized material. No other reflections were obtained under these conditions over a range of Bragg angle of 0 to 45° using either type of specimen. As a consequence, the intensity of the (200) reflections from the rolling plane was taken to indicate the amount of recrystallized material present in a specimen, and the corresponding intensity of the (220) reflections was taken to indicate the amount of unrecrystallized material present.

To insure flatness and proper alignment of the reflecting specimen in the spectrometer, the sample was laid in a slot ½ in. wide x 0.001 in. deep which was machined in a ¾x2x½ in. steel carrier. The specimen then was taped down with cellophane tape. This steel cradle was mounted vertically in the specimen holder of the spectrometer so that the bottom edge of the carrier rested against a horizontal shoulder.

Intensity data used in plotting the percent of recrystallized material vs. time at temperature were obtained by directly counting the diffracted beam of nickel filtered copper K $\alpha$  radiation used throughout the work.

The X-ray spectrometer was employed also in obtaining pole figure data to be used for orientation determinations. At the beginning of this investigation a transmission pole figure holder was used.<sup>5</sup> As a thickness of 0.002 in. of this alloy was found to be opaque to the copper K $\alpha$  radiation, it was necessary to reduce the thickness of the pole figure specimen. A cold-worked sample was etched in a 50 pct HCl solution for 5 min and was found to transmit a

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This paper is part of a dissertation to be submitted by W. E. Seymour to the faculty of the Metallurgy Department of Rensselaer Polytechnic Institute in partial fulfillment of the requirements for the degree of Doctor of Philosophy.



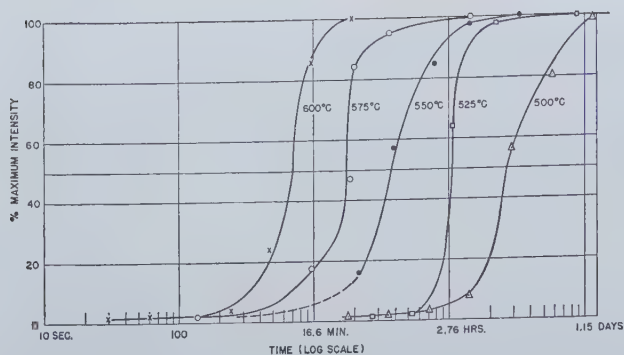


Fig. 1—Increasing intensity of (200) reflections as a function of time at indicated temperature.

strong beam when mounted in position in the pole figure holder. It was found that the etching had reduced the sample thickness from 0.002 in. to approximately 0.0015 in., and had heavily pitted the surface. The Geiger counter was rotated to the proper Bragg angle for measuring (111) reflections, and these data are plotted in fig. 5.

A reflection pole figure holder<sup>5</sup> was used for all other pole figure work. This eliminated the necessity for correcting diffracted intensities for differences in path length<sup>8</sup> through the specimen, as was necessary when using the transmission pole figure holder, and also made it unnecessary to reduce the thickness of specimens by etching. The (111) transmission pole figure for the cold-worked material was checked using the reflection method and good agreement was obtained. Data for the (100) pole figure were also obtained for the cold-worked material (fig. 6), as well as data for the (100) and (110) pole figures of a sample recrystallized 100 pct at 500°C (figs. 7 and 8).

For metallographic study, longitudinal sections of the various specimens were mounted in Selectron (to avoid heating), polished, and etched with two parts of 20 pct HCl and one part of 3 pct H<sub>2</sub>O<sub>2</sub>. This etchant revealed the crystal boundaries and developed etch pits<sup>9</sup> within a grain indicating its orientation.

"Tukon" microhardness measurements were made on all specimens heat treated at 500° and 600°C, using a 100-g load. An average of ten readings was taken per specimen. These data were plotted vs. log time for each temperature (fig. 4) and compared with the reaction rate curves plotted from the X-ray intensity data.

### Results and Observations, Reaction Kinetics

In fig. 1 are plotted the data obtained by counting the intensities of the (200) reflections from each specimen. These intensities indicate the amount of recrystallized material in the specimens, and are plotted (as percent of maximum intensity) for each temperature. It was assumed that 100 pct recrystallized material was present when the (200) reflected intensity remained constant from specimen to specimen with increasing time at temperature. The ordinate of fig. 1 can therefore be interpreted as percent recrystallized material present.

Fig. 2 is a similar plot expressing the disappearance of the (220) reflections (cold-worked or deformed material) as a function of time for the same temperatures as in fig. 1. The time for 50 and 100 pct recrystallization at each temperature as determined from the curve of the intensity of (200) reflections vs. log time checks well with the corre-

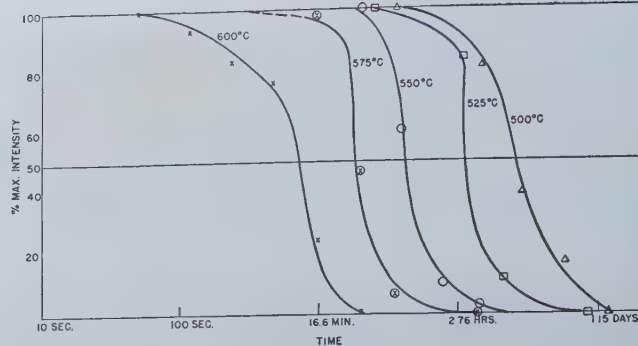


Fig. 2—Decreasing intensity of (220) reflections as a function of time at indicated temperature.

sponding times determined from the curve for intensity of (220) reflections vs. log time. This can be seen from a comparison of figs. 1 and 2.

It is interesting to note that the X-ray data indicate complete recrystallization at as low as 500°C. Complete recrystallization can also be expected at lower temperatures, if longer times are used.

The data obtained show the recrystallization reaction to be extremely temperature sensitive, requiring approximately 32 hr for completion at 500°C as contrasted with only 32 min at 600°C.

The activation energy for the reaction was calculated, using the curves of fig. 1, by plotting log time for 50 pct reaction vs.  $1/T$  ( $T$  in °K). Consider the Arrhenius formula, rate =  $Ae^{-\Delta E/RT}$ . It can be seen that  $e^{-\Delta E/RT}$  is inversely proportional to the time for a given amount of reaction, and there-

$$\text{fore we may obtain } \log t_c = \frac{\Delta E}{2.3R} \frac{1}{T} + \log B,$$

where:  $t_c$  = time for reaction to give a concentration  $c$ .

$\Delta E$  = activation energy for reaction in cal/mol.

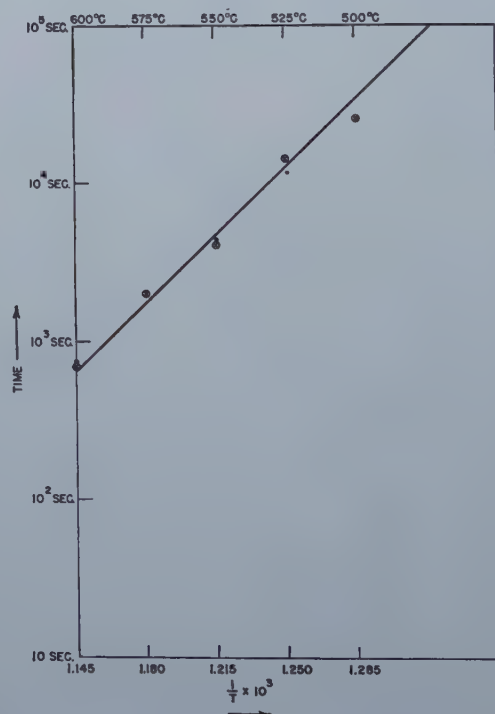


Fig. 3—Log time for 50 pct recrystallization vs. reciprocal of absolute temperature.

Black dots are points obtained from fig. 1. Circled crosses are points taken from fig. 2.



$R$  = gas constant.  
 $T$  = temperature in  $^{\circ}\text{K}$ .  
 $B$  = a constant.

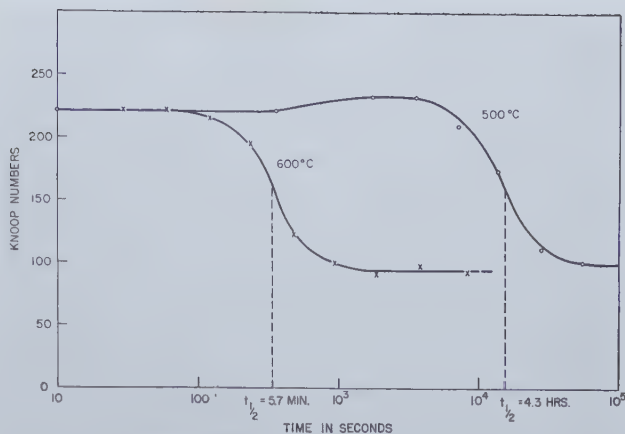
and all logarithms are to the base 10.

This formula is in the form of the slope-intercept equation for a straight line ( $y = mx + b$ ), where  $\Delta E/2.3R$  is the slope,  $\log t_0$  is the ordinate and  $\log K$  is the intercept on the ordinate axis when  $1/T$  is zero. A plot of  $\log t_{1/2}$  against  $1/T$  appears in fig. 3. The slope was evaluated and equated to  $\Delta E/2.3R$ , and  $\Delta E$  was found to be 56,500 cal/mol. This figure is of the same order of magnitude as that for a diffusion process. (The activation energy for the diffusion of nickel in iron is reported to be 64,000 to 68,000 cal/mol<sup>17</sup>.)

Fig. 4 shows plots of Tukon microhardness against log time for the 500 $^{\circ}$  and 600 $^{\circ}\text{C}$  specimens. When these curves are compared with figs. 1 and 2, it appears that 50 pct recrystallization, as measured directly by X-ray diffraction, produces about 85 pct of the hardness change on annealing. Possibly this may mean that the indenter pushes the harder unrecrystallized areas into the softer recrystallized material surrounding them, thus decreasing the resistance to the penetration of the indenter at a greater rate than the actual volume increase in recrystallized material.

### Orientation Determination

Stereographic projections showing the concentration of (111) and (100) poles of the cold-worked material—that is to say, pole figures for (111) and (100)—are presented, respectively, in figs. 5 and 6. In these figures, the intensities are represented by the diameters of the circles. In all the pole figures only the solid lines represent actual data. The dotted lines were drawn from the symmetry of the structure. Using figs. 5 and 6, three crystallographic orientations may be determined as existing simul-

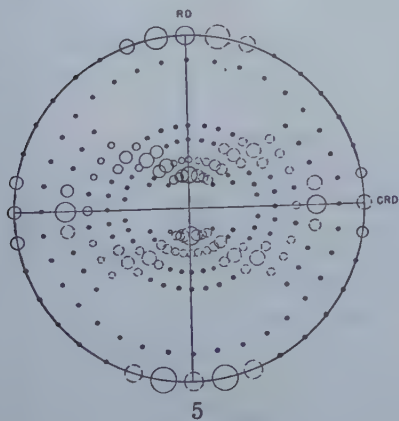


**Fig. 4—Tukon microhardness in Knoop numbers vs. time at 500 $^{\circ}$  and 600 $^{\circ}\text{C}$ .**

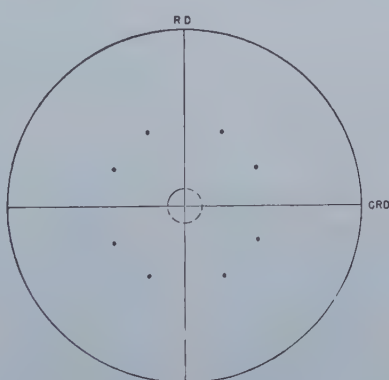
A 50 pct total change in hardness corresponds to a time of 5.7 min at 600 $^{\circ}\text{C}$  and 4.3 hr at 500 $^{\circ}\text{C}$ .

taneously in the cold-worked material, namely, in decreasing order of importance, (112)  $[\bar{1}\bar{1}1]$ , (110)  $[\bar{1}12]$ , and (123)  $10^{\circ}$  from  $[\bar{3}12]$ . Data for (100) and (110) pole figures were obtained from a specimen completely recrystallized at 500 $^{\circ}\text{C}$ ; these are presented in figs. 7a and b and 8. The poles of the form {100} are highly concentrated in the rolling, cross rolling, and sheet normal directions, the maximum variation being  $\pm 10^{\circ}$  from (100)  $[001]$ .

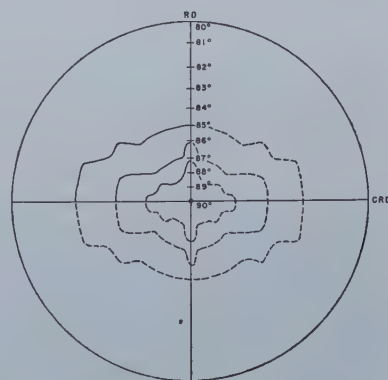
What appeared to be small twinned areas were occasionally observed under the microscope in the samples recrystallized at 500 $^{\circ}\text{C}$ . To check this observation, the positions of (001) and (110) poles of material twinned by reflection across (111) were calculated<sup>8</sup> and these regions of the pole figure investigated by means of the X-ray diffraction spectrometer. Slight increases in intensity at two such points were observed and accepted as indicating the presence of 1 to 2 pct twinned material in the



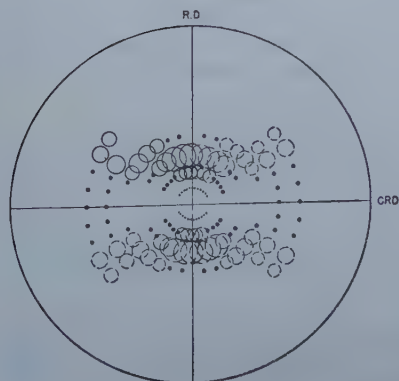
5



7a



7b



6

**Fig. 5—(111) pole figure "as-rolled" structure.**

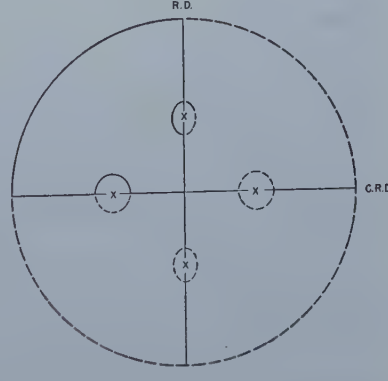
**Fig. 6—(100) pole figure "as-rolled" structure.**

**Fig. 7a—(100) pole figure, 100 pct recrystallized texture.**

Black dots represent location of observed twin poles.

**Fig. 7b—Fine scale distribution of (100) poles in recrystallized texture.**  
 (100) poles distribution in a  $\pm 10^{\circ}$  stereographic area.

**Fig. 8—(110) pole figure, recrystallized texture.**



8



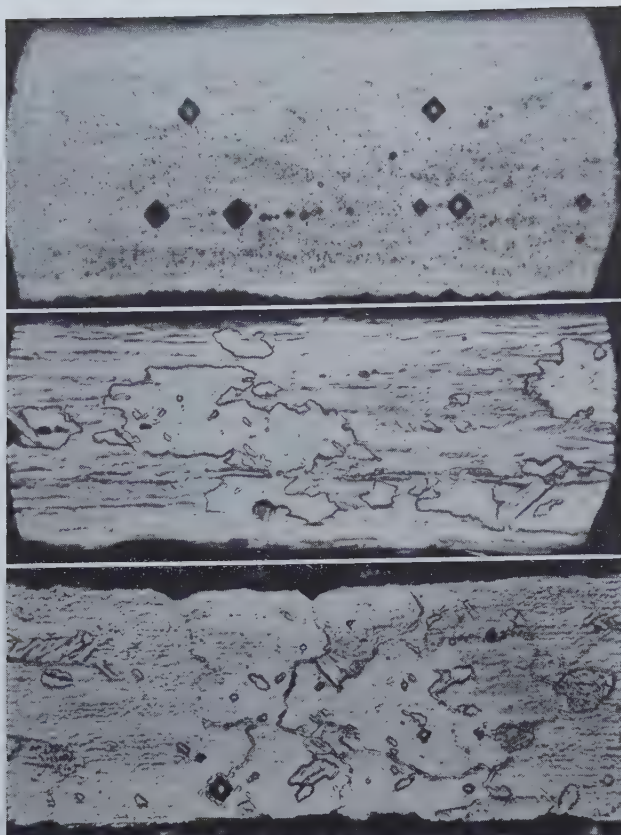


Fig. 9a—Etch pits in "cube texture," 50 pct iron 50 pct nickel alloy.

Annealed 1 hr at 1050°C. Longitudinal section. X1500. Area reduced approximately two thirds in reproduction.

Fig. 9b and c—Micrographs showing progress of recrystallization at 500°C.

b—25 pct recrystallized material. 4 hr at 500°C. Longitudinal section. X1500. Area reduced approximately two thirds in reproduction. c—100 pct recrystallized material. 72 hr at 500°C. Longitudinal section. X1500. Area reduced approximately two thirds in reproduction.

specimens. The positions of the two twin poles so observed are indicated by black dots in the pole figure illustrated in fig. 7a.

### Metallography

An etchant consisting of two parts of 20 pct HCl and one part of  $H_2O_2$  in water was applied for approximately 10 sec with a swab.

Micrograph 9a illustrates the square etch pits obtained in a longitudinal section of a specimen from a different heat, when annealed 1 hr at 1050°C. The diagonals of the square etch pits at the specimen surface are observed to be in the direction of rolling. The etch pits were observed to be square pyramids such as would be formed by the intersection of four {111} planes with the surface of the specimen. Micrographs 9b and c illustrate the progress of recrystallization at 500°C. Fig. 9b represents approximately 25 pct recrystallization (4 hr at 500°C, fig. 2), and 9c shows 100 pct recrystallization (70 hr at 500°C). The etch pits, which indicate the "cube texture," can be observed in the latter picture.

What is taken to be twinned material can be observed in 9c as areas within the larger crystals; in many instances with boundaries at approximately 45° to the direction of rolling.

An idea of the difference in grain size obtained by conventional recrystallization practice of 1 hr at

1050°C and that observed after 72 hr at 500°C can be obtained by comparing 9a and c. The area shown in a is from a single crystal, the boundaries of which extend far beyond the microscope field at that magnification, while a number of grains are evident in c. The rate of grain growth, after recrystallization, is assumed to be retarded at the lower temperature.

### Summary and Conclusion

1. Data for the kinetics of the recrystallization reaction in a 98 pct cold reduced 50 pct iron-nickel alloy were obtained with an X-ray spectrometer. Curves showing the amount of material transformed, were plotted against log time at temperatures from 500° to 600°C. At 500°C, 100 pct recrystallization occurred in 32 hr, and at 600°C in 32 min. These results showed the reaction to be very temperature sensitive in this range.

2. Curves of hardness vs. log time at temperature showed an 85 pct total softening at only 50 pct recrystallization for 500° and 600°C.

3. The heat of activation for the recrystallization reaction in this alloy was found to be 56,500 cal/mol. This is of the same order of magnitude as the activation energy for the diffusion of nickel in  $\gamma$  iron (64,000 to 68,000 cal/mol).

4. A multiple crystallographic orientation was found in the cold-worked material. Two principal orientations exist: (112)  $[\bar{1}11]$ , and (110)  $[\bar{1}12]$ , the former predominating. A third—though somewhat minor—orientation was also found, which was approximately (123)  $10^\circ$  from  $[\bar{3}12]$ .

5. The orientation after complete recrystallization at 500°C was determined by means of etch pits and pole figures, and found to be a typical "cube texture," (001)  $[100]$ , with a maximum spread of  $\pm 10^\circ$  from the rolling plane and rolling direction.

6. Slight twinning was observed in recrystallized areas under the microscope. Positions of the twin poles assuming twinning by reflection across (111) were determined by calculation and checked experimentally. An estimated 1 to 2 pct of twinned material was found.

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# Production and Examination of Zinc Single Crystals

by D. C. Jillson

This paper describes a method and equipment developed and used for the growth of single crystals of high purity zinc, of substantial size and of various orientations, in substantial numbers, together with the results of some tests of the degree of perfection of the product.

**B**RIDGMAN<sup>1, 2</sup> melted metals in a graphite or hard glass tube and lowered the tube through a furnace to make it cool from one end only. Because of the difficulty of eliminating all vibration of the mold, others have raised the furnace instead. Neither way seems as desirable as a setup with no motion of either the mold or the furnace. A furnace in which both the shape and the slope of the temperature gradient could be controlled and varied over a wide range and in which such a gradient could be moved from one end of the furnace to the other, freezing the specimen from one end to the other, at any desired rate, all by means of isolated external control, seemed to offer definite advantages. In addition to eliminating the possibility of vibration due to moving parts, it might also give better control over the direction and rate of heat flow.

Such an apparatus was assembled and is shown schematically in fig. 1.

## Equipment

**Furnace:** A clay-carborundum tube of 3½ in. ID with a ½ in. wall thickness was used as the core. This had a main winding of No. 12 B.&S. gauge Nichrome V with some compensation for heat loss at the ends. Taps to this winding were made at points 12 in. from each end. Fig. 2 shows details of this winding and of the two end windings. Each end winding was wound over Micanite over the main winding. No. 15 B.&S. gauge Nichrome V was used for these, and again taps were supplied at two intermediate points on each. The tube was supported in an 18 in. OD black iron shell with brick insulation. The input to each of the windings was regulated by means of a variable transformer.

**Temperature Regulation:** A chromel-alumel thermocouple located near the furnace wall in the

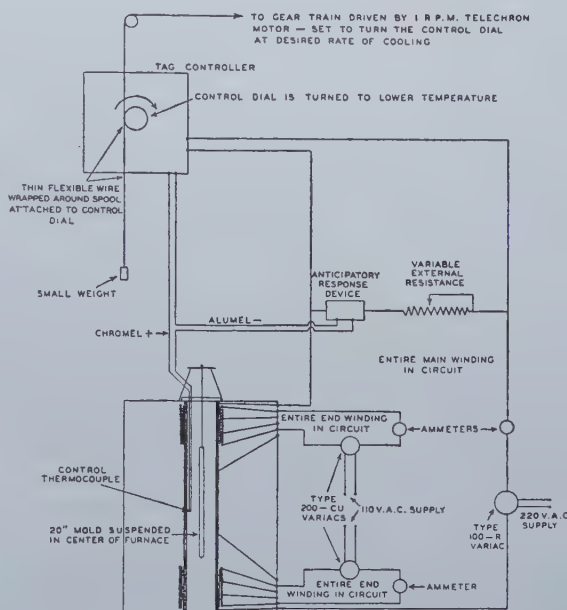


Fig. 1—Schematic drawing of equipment for growing single crystals.

center of the furnace was connected with a Celec-tray controller, type PIC, 300° to 900°C range, which opened and closed a shunt across an external variable resistance in the main winding circuit. An "anticipatory response" device also was incorporated to minimize the cyclic effect of the control mechanism.

Eleven survey couples in a common pyrex glass protection tube were located near the furnace wall and spaced 2 in. apart. The couple leads went to a common reference junction box where they were connected to copper leads from a selector switch which, in turn, was connected to a type K potentiometer. This arrangement permitted rapid temperature surveys.

The knob on the controller dial was replaced with a threaded brass spool turned at a controlled rate by a thin iron wire one end of which was attached to a gear train and the other to a small weight heavy enough to prevent slipping of the wire on the spool. The gear train, driven by a 1-rpm Telechron motor, contained a series of different sized interchangeable gears and threaded drums permitting a range of travel speeds from 0.10 in. per hr up to a hypo-

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thetical 108,000 in. per hr. This arrangement afforded a controlled linear rate of cooling of the furnace (limited by the ability of the furnace to dissipate heat).

**Molds:** Precision-ground pyrex glass tubing was the material usually used for molds. Constrictions in ordinary pyrex tubing caused deformation of the specimens during cooling and hindered removal without further deformation.

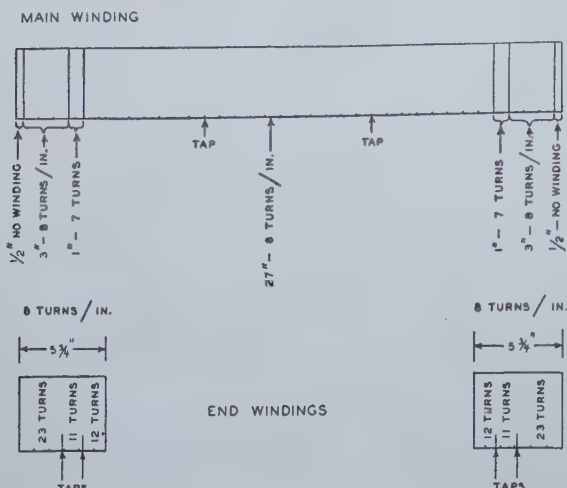


Fig. 2—Plan showing dimensions and number of turns per inch of the main and end windings of the single crystal furnace.

The tubes were sealed to a point at one end. A blunt, almost square end with a tiny point or tit in its center gave better results than a long tapered point. They were cleaned in potassium dichromate-sulphuric acid cleaning solution and rinsed with distilled water. Then, the inside of each tube was coated with a thin layer of semicolloidal graphite to prevent the zinc from adhering to the glass.

### Typical Procedure

Seven molds, 1/2 in. ID and 21 in. long, wired together, were lowered into the furnace, slowly enough to prevent cracking of the tubes from heat shock, until the tops of the tubes were even with the top of the furnace, which was controlled at about 500°C. Molten zinc was skimmed and poured through a heated pyrex funnel into the molds, which were then lowered into position.

The analysis of 99.999+ pct zinc used was as follows, in per cent: lead, 0.00013; iron, 0.0006; cadmium, 0.00003; and copper, 0.00012. No tests were made for A, Br, Cl, F, He, H, I, Kr, Ne, N, O, Se, S, Xe. Other elements were not detected or were in insignificant amounts. Total impurities detected were 0.00088 pct.

A few crystals were grown of 99.99+ pct zinc, which analyzed, in per cent: lead, 0.0025; iron, 0.0011; cadmium, 0.0018; and tin, <0.0001. Total impurities were 0.009 or less by specification.

The top of the furnace was closed, the current into the main and end windings was set to obtain a temperature gradient of 8°C per inch, and the furnace was allowed to come to equilibrium with the control dial set at 514°C.

The current settings were as follows: Main winding, high current, 5.3 amp.; and low current, 2.8 amp. Top winding, 3.2 amp. Bottom winding, 1.4 amp.

When the furnace temperature had reached equilibrium, a temperature survey was made (fig. 3).

The gear train was set to move the brass spool on the control dial at a rate of 0.15 in. or 7.4°C per hour, and the motor was started. Temperature surveys were made at 2-hr intervals. Fig. 3 shows how the gradient moved through the furnace. When it had reached a position such that all of the zinc was frozen, the top of the furnace was opened and the seven tubes were removed and permitted to cool in air.

When the specimens had cooled to room temperature, they were removed from the molds, etched in 50 pct hydrochloric acid for 5 sec, rinsed with water and then with alcohol, and dried in air. This etching cleaned the surface and brought out bright reflections from the first order zones of the crystal lattice. Very great care was required to avoid deformation in handling.

### Temperature Gradient and Cooling Rate

When the temperature gradient was below 5 1/2°C per inch, polycrystalline material resulted. Above this, up to 13 1/2°C per inch, single crystals were obtained. Single crystals were grown with a cooling rate as low as 5°C per hour. When the cooling rate approached 40°C per hour, polycrystalline material sometimes resulted. For most of the specimens grown, a temperature gradient of about 8°C per inch and a cooling rate of 7.4°C per hour were used. The yield of single crystals with these conditions was essentially 100 pct.

### Description and Examination of Specimens

**Shapes, Sizes, Analyses:** About 200 specimens of various shapes and sizes up to 1 1/2 in. diam and 19

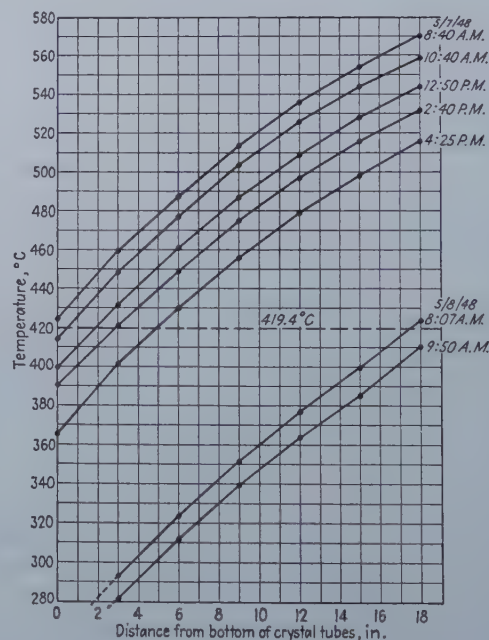


Fig. 3—Single crystal run No. 7.

Gear train started at 8:43 A.M., May 7, 1948. Specimens removed from furnace at 10:00 A.M., May 8, 1948.

Note: Seven survey couples, spaced 3 in. apart, were used in this run, but, in a later built furnace, 11 couples spaced 2 in. apart, were used.

in. in length were produced. Spectrographic analyses of specimens showed no increase in any impurity contents within the limits of detection.

**Determination of Orientations:** For many purposes, orientations could be determined with sufficient accuracy from markings produced by cleavage, slip, twinning, etc.



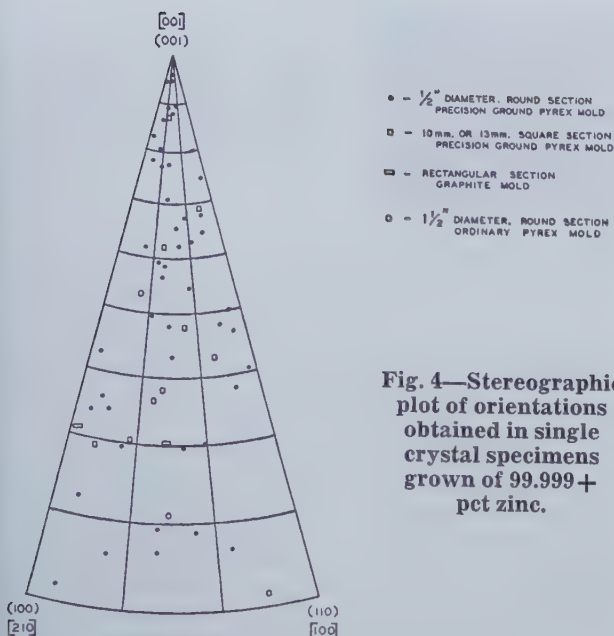


Fig. 4—Stereographic plot of orientations obtained in single crystal specimens grown of 99.999+ pct zinc.

where near the specimen axis. This seemed consistent with the ideas that zinc crystals grow more readily in a direction parallel to the basal plane<sup>4, 5</sup> and that the principal direction of heat flow was along the axis of the specimen. In the present moving-gradient furnace, it was felt that the heat flow was more lateral and that the basal planes of the specimens grown might tend to be perpendicular rather than parallel to the specimen axis. This seemed to be borne out in a few specimens prepared with 99.99+ pct zinc, eight out of eleven specimens being within 20° of perpendicular, but in specimens of 99.999+ pct zinc the orientations seemed to be reasonably random, as shown in the stereographic plot of fig. 4.\* A larger number of carefully oriented

\* Three-coordinate Miller indexes are used in fig. 4 and elsewhere in this paper.

specimens should be subjected to statistical analysis before definite conclusions are drawn, but the present limited data suggest a possibility that preferred directions of crystal growth in zinc crystals may be influenced by very small amounts of impurities. Straumanis<sup>6</sup> reported such an effect for appreciable amounts of cadmium.

**Tests of Perfection: Visual Examination of Surfaces of Specimen:** Light etching in 50 pct HCl revealed no gross departures from perfection in properly grown single-crystal specimens. Constrictions in molds, jarring, differential thermal contraction in multi-crystal specimens, and, of course, deformation in handling did cause observable imperfections.

Buerger<sup>7</sup> stated that zinc single crystals grown by the Bridgman method from 99.9+ pct zinc are internally partitioned by discontinuities in such a way that the entire structure is continuous but branched, and that etching exhibits essentially filled-in dendrite frameworks or lineages. He noted that Straumanis<sup>6, 8, 9</sup> had given etching evidence of what appeared to be lineage structure in zinc single crystals grown from melts under various conditions. Buerger also made observations on the lineaged nature of crystals grown from 99.999+ pct zinc. In the present work, specimens of 99.999+ pct Zn etched with 50 pct HCl showed no marked dendritic structure covering the cylindrical surface. Furthermore, the etching pattern on a cleavage surface was different from the mosaic on Buerger's 99.9+ pct or 99.999+ pct zinc specimens, and prolonged etching tended generally to eliminate definite markings on such surfaces.

Deep etching with 50 pct hydrochloric acid—for example, a 5 to 10-min treatment—did give ridges on the cylindrical surface on one side, found to be the last side to freeze, of several specimens of 99.999+ pct purity, as shown in fig. 5. These were shown to be areas of lead concentration in dendrite boundaries. It would appear that the lead content of the purest zinc used (0.00013 pct) was greater than the solid solubility limit (which is probably not greater than 0.00008 pct, on the basis of analysis of the unridged portion). With zinc of higher lead content (99.99+ pct zinc, 0.003 pct Pb maximum), deep etching gave ridges on all sides of the specimen.

Straumanis<sup>6</sup> found similar ridges on etched single crystals of zinc containing cadmium. The nature and degree of these ridges varied with the cadmium content, and he concluded that they were due to the cadmium. He found the ridges to be parallel to the basal plane and concluded that, in general, impurities present in excess of their solid solubility limit

For greater accuracy, a simple light-reflection method could be used sometimes which was based on the observation that cylindrical single crystal rods lightly etched with 50 pct HCl gave bright reflections from the zones of first order pyramids and prisms. The specimen was mounted on a horizontal specimen holder and a simple one-circle goniometer was fixed on one end with the zero reading at a reference mark on the specimen. A horizontal beam of light was directed by a "vertical illuminator" to strike the specimen at a measured angle to the specimen axis. Light reflected by the specimen back through the illuminator played upon a photometric cell connected to a galvanometer. The galvanometer deflections produced by this light were observed by means of a spot of light reflected from the galvanometer mirror to a scale on the wall. As the specimen was rotated about its axis, the points of maximum light reflection were determined and recorded to the nearest half degree. Sets of readings at five different angles to the specimen axis served to determine the first order zones with an accuracy limited primarily by the accuracy of the angular settings. Errors in these settings could be minimized by merely increasing the number of settings or by rotating the specimen holder upon a goniometer stage. A simple stereographic plotting of the first order zones, of course, gave a complete determination of the orientation. Different etchants brought out reflections from different planes or zones of planes. For example, zinc single crystals etched with a chromic acid-sodium sulphate reagent gave brighter reflections from second order zones than from first order zones. The length of the etching treatment also was a factor.

In cases where it was desired to eliminate unintentional deformation as completely as possible, standard X-ray back-reflection Laue methods were used because they involved less handling. Results were determined both by plotting stereographically the actual Laue spots and by plotting zones of spots as suggested by Greninger.<sup>8</sup> It was concluded that the latter method is faster and at least as accurate.

Previous work in The New Jersey Zinc Co. (of Pa.) laboratories, growing single crystals of 99.99+ pct zinc by the usual Bridgman method of lowering a mold through a furnace, had seemed to indicate some preference for the basal plane to lie some-



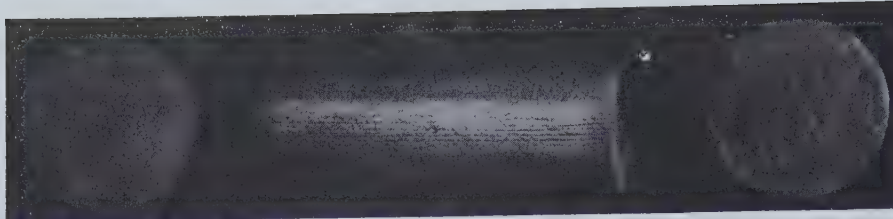


Fig. 5—Ridges produced on single crystal of 99.999+ pct zinc by deep etching with 50 pct HCl (approximately X2).

at the freezing point tended to separate in layers parallel to the basal plane. He found some similar ridges on etched single crystal specimens of Kahlbaum zinc, but thought that the small amount of cadmium present (probably 0.03 pct) could not be responsible for these. It might be pointed out that in Straumanis' specimens the basal plane was parallel to the specimen axis, as were also the ridges from etching, that this might be a chance coincidence, and that the ridges might not necessarily be parallel to the basal planes. In the present case, ridges were observed parallel to the specimen axis when the basal plane was practically perpendicular to it.

Deep etching with 50 pct HCl also showed preferential attack in certain crystallographic directions. Specimens with the basal plane approximately perpendicular to the rod axis tended to become six-sided, the tendency being toward a second order prism. Sometimes small prism faces between first and second order faces also appeared.

**Examination of Cleavage Surfaces:** Freshly prepared basal cleavage surfaces were examined for evidences of departure from crystalline perfection. It was impossible, however, to cleave without deforming the cleavage face, and it was felt that all of the imperfections observed could have been and probably were the result of deformation rather than of imperfect crystal growth. Conditions of cleaving which reduced the amount of accompanying deformation always reduced the amount of these markings. It was noted also that there was a distinct tendency for specimens to hold together at the surface even when cleavages through the bodies of the specimens were otherwise quite complete. Greenland<sup>10, 11</sup> has observed the same phenomenon with single crystals of mercury.

Light etching with 50 pct HCl (1 sec) caused etch pits that were hexagonal in nature, usually shallow hexagonal pyramids, and always of the second order. These were not considered necessarily indicative of crystalline flaws, although it is possible that they may have tended to originate at imperfections. They definitely did tend to concentrate, in many cases, on mechanical imperfections resulting from deformation, perhaps not on *twins*, but definitely in [210] or second-order directions (perhaps on bends) and probably on tear marks and light scratches, and probably in areas of lead concentration. Perhaps all pits originated at lead (or other impurity) particles. The pits originating at mechanical flaws may have started at particles precipitated from solid solution by mechanical stress or strain. Sometimes light markings having the appearance of dendrite boundaries were seen—not associated with the hexagonal etch pits.

With very deep etching (5 to 10 min) a deep dendritic pattern appeared in the area of lead concentration, as noted above on the specimen surfaces (see fig. 5).

**X-ray:** X-ray back-reflection Laue diffraction patterns were prepared from the cylindrical surface of specimens and also from cleavage surfaces. Orienta-

tions calculated from reflections from the opposite ends of each of several specimens indicated no significant difference in orientation from end to end.

Back-reflection spots from undeformed material were apparently just as perfect as those given by the beam itself.

### Summary and Conclusions

A moving-gradient apparatus was contrived in which single crystals were grown from molten metal without motion of either the mold or the furnace. Conditions were determined that gave a high yield (essentially 100 pct) of single crystals of zinc, and about 200 specimens of various shapes and sizes up to 1½ in. diam and 19 in. in length were produced. Using zinc of 99.999+ pct purity, crystals were produced that appeared to be at least as perfect as any described in the literature and probably better than most.

Etching experiments yielded new information regarding the solid solubility of lead in zinc and revealed certain characteristics of the attack of hydrochloric acid (50 pct) on zinc of 99.999+ pct purity.

### Acknowledgments

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# An Experimental Survey of Deformation and Annealing Processes in Zinc

by D. C. JILLSON

Zinc single-crystal specimens of high purity and quality were used in a study of various types of deformation under various conditions. Deformed specimens were annealed to study recovery and recrystallization. New data are presented and previous data are correlated and evaluated in order to determine profitable areas for more detailed work.

WORK in recent years<sup>1-4</sup> has indicated a complexity of the processes of deformation of metal crystals not previously appreciated and not fully accounted for by any hypothesis so far advanced. Furthermore, the nature and mechanism of formation of nuclei of recrystallization have not been determined precisely. The deformation of single crystals of zinc has been studied frequently, but the purity of the zinc and the perfection of the specimens sometimes have been given little consideration. Methods have been developed recently that readily yield zinc single-crystal specimens of high quality.<sup>5</sup> In the present work, such specimens were deformed in various ways under various conditions, and deformed specimens were annealed to obtain information regarding recovery, recrystallization, and grain growth. The paper attempts to correlate and evaluate previous data, as well as to present new data, in order to determine areas in which more detailed work might be done most profitably.

Tests at temperatures from the freezing point (419.46°C) to room temperature revealed glide only on basal planes in a close-packed direction [100]\*,

\* Planes and directions will be designated by three-coordinate Miller indexes. Parentheses and brackets will be used to designate families as well as particular planes or directions.

as reported by Mark, Polanyi, and Schmid<sup>6</sup> and others. Markings probably similar to those observed by Kolesnikov<sup>7</sup> and Boas and Schmid<sup>8</sup> were noted in specimens stretched at elevated temperatures, but it seemed clear that these were not caused by prismatic or pyramidal slip (see second paragraph of section on Phenomena Involving Bending of the Basal Plane).

## Twinning

Twinning on the octahedral plane of a face-centered cubic metal has been pictured as a process of simple homogeneous shearing along that plane in a [112] direction. It was recognized by Mathewson and Phillips<sup>9</sup> and others<sup>10-15</sup> that the (102) twinning of zinc required a somewhat more complex mechanism and might be considered as a homogeneous shearing of (102) planes in a [211] direction plus slight adjustments of atoms to positions of greater stability or lower energy, or as a single movement of each of the atoms in the same sense into the final

positions. Gough and Cox<sup>14</sup> modified Mathewson's mechanism to obtain a more stable lattice configuration, but it is not clear that they succeeded, and their mechanism requires movement of some of the atoms in a sense opposite to that of the overall twinning movement. They also suggested that twinning may occur as a result of previous basal slip. This conclusion was based on the observation that twinning caused by alternating torsion was clearest and most profuse at positions for maximum basal slip rather than for maximum stress on (102) planes in the close-packed direction (not the twinning direction), and no mechanism was described. It might be wondered whether resolution of stresses on the twinning plane in the twinning direction would have afforded a simpler explanation.

If twinning is essentially a simple homogeneous shearing along the twinning plane, it would seem that twins should grow by a smooth, continuous mechanism, and, indeed, that a simple reversal of stresses should reverse the shearing and de-twin the crystal. Cylindrical tablets  $\frac{1}{8}$  to  $\frac{1}{4}$  in. thick were cleaved from single-crystal specimens and were squeezed, perpendicular to a second-order prism plane, to give a tensile stress perpendicular to a first-order prism plane. A "click" was heard and a thin, needle-like twin appeared on the basal cleavage face. If squeezing was continued smoothly, the twin, viewed at magnifications up to X500, grew smoothly and quietly (fig. 1). X-ray examination verified that the twinning was of the (102) type. Rotating the compression axis 90° to reverse the stress then caused a smooth, continuous shrinkage and ultimate disappearance of the twin (fig. 2). The squeezing also caused a rumpling of the basal

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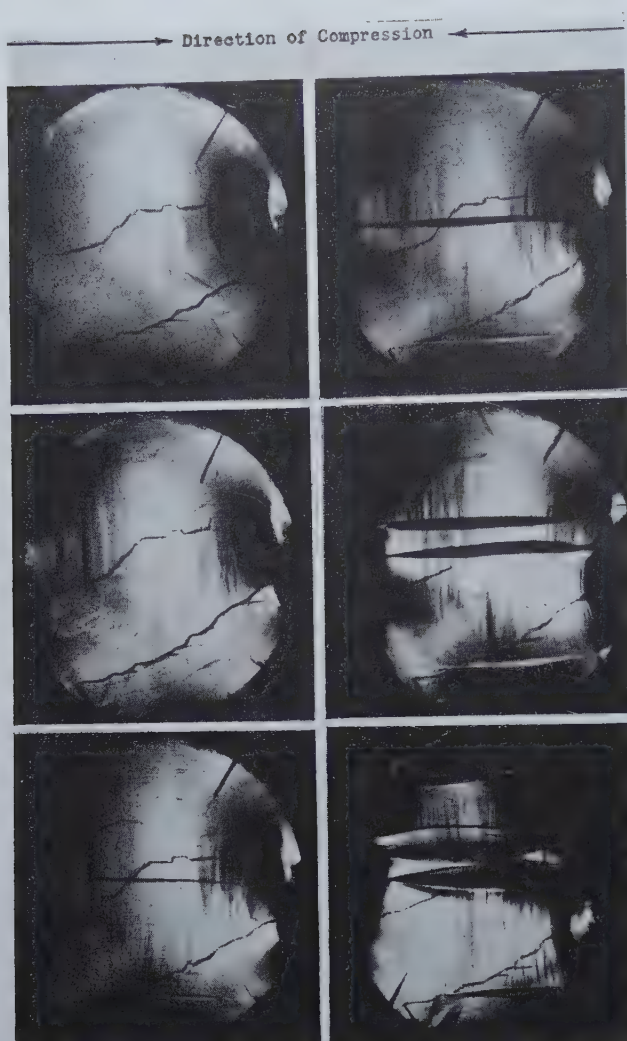


Fig. 1—Steps in growth of twins in single-crystal tablet of zinc (diam  $\frac{1}{2}$  in.).

cleavage faces which preceded and accompanied twinning but is not believed to be a part of the twinning process (see third paragraph of next section).

Twins, it was believed, should start with the formation of a layer only one identity period (4 atom layers) thick. Since the registry between this twinned lattice and the parent lattice on both sides is imperfect, this must change the crystal from a condition of minimum energy to one of higher energy, the difference residing in the boundaries. This done, the twin could grow in thickness simply by transferring atom layers from perfect registry with the parent crystal to perfect registry with the twin, requiring less energy and a lower shearing stress than was necessary to form the original twin. Of course, a twin only one identity period thick must be rather unstable under the combined influences of the two parts of the parent lattice so near to each other, and the stress required for growth probably will not drop to a constant value until the twin is wide enough so that neither boundary will be affected by the other. Now, if a high stress is required for formation and is relieved only slightly by the very small change in dimensions accomplished, the residual stress might be higher than the minimum required for growth, and growth might proceed very rapidly until the stress drops to the critical value. This could account for the apparently in-

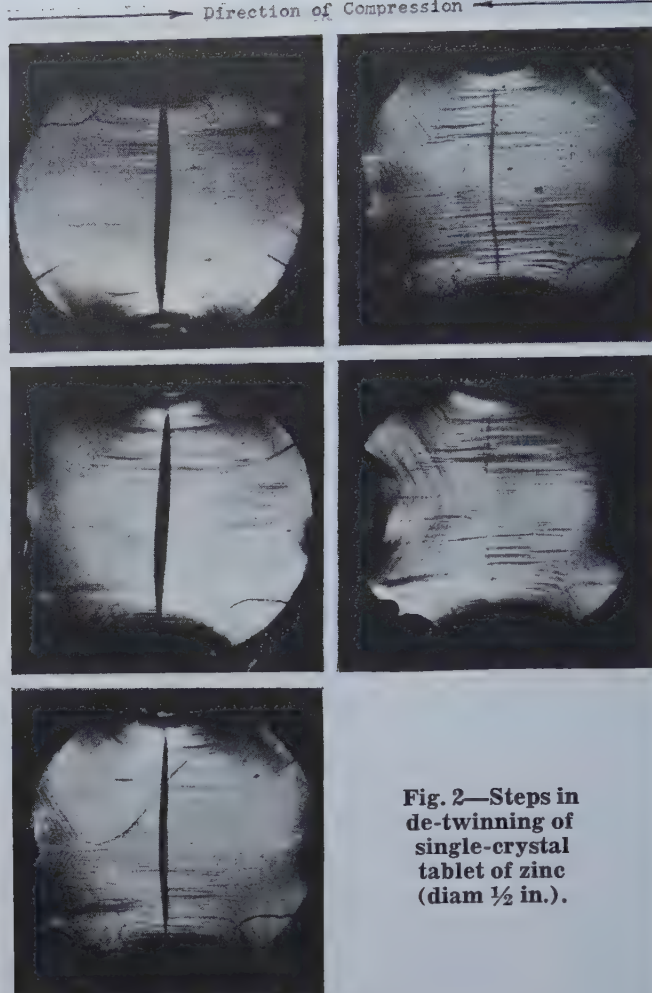


Fig. 2—Steps in de-twinning of single-crystal tablet of zinc (diam  $\frac{1}{2}$  in.).

stantaneous formation of twins much thicker than one identity period. It is a corollary that, in de-twinning, as the twin approaches the identity period in thickness it should de-twin more rapidly or at a lower stress.

In order to slow down the twinning and de-twinning processes for closer study, high speed motion pictures of these phenomena were prepared, using the Eastman High Speed Camera. The photographic work was done by Technalysis, Inc., of Philadelphia, Pa. Speeds as high as 3000 frames a second were used. Projection at a speed of 16 frames a second suggested, and frame by frame analysis of some of the films (fig. 3) verified, that both the initial rate of growth and the final rate of de-twinning were very rapid, as predicted. The data of fig. 3a suggest a step-like relationship, but it is believed that this is caused by experimental aberrations and that the smooth curve more nearly represents the true conditions. With improved techniques, particularly if stress determinations and analyses could be included, this method of study might prove to be very useful.

#### Phenomena Involving Bending of the Basal Plane

Examination of a basal cleavage face of a single crystal of zinc rather severely deformed by stretching, bending in various directions, and straightening showed, in addition to three sets of (102) twin markings, three sets of striations of a different character (fig. 4), two essentially perpendicular and one essentially parallel to twin bands. Previous investigators,<sup>16-20</sup> noting similar markings, have sometimes



attributed them to second-order pyramidal or prismatic slip or to second-order twinning. This would not, however, account for the striations parallel to (102) twins in fig. 4. Furthermore, all three sets of striations in fig. 4 were similar in appearance and unlike the (102) twins.

Miller<sup>19,21</sup> showed clearly the presence of a "bend" plane between areas of greater and less deformation (by basal slip) in zinc single crystals. Similar bends were noted in the present investigation, particularly in specimens stretched at elevated temperatures. The bend plane bisected the angle between the basal planes of the two parts of the crystal and cut the basal planes at right angles to the slip direction. In other words, the bend in each basal plane was about a second-order trace, or a [210] direction. When the bend was slight, the bend plane was almost perpendicular to the basal plane, and it seems likely that it was markings of this type that Kolesnikov<sup>7</sup> and others have taken as indications of prismatic or pyramidal slip. Greenland<sup>22</sup> observed similar markings in single crystals of mercury, Gough and Cox<sup>15</sup> in zinc, and Andrade and Tsien<sup>23</sup> in sodium. There was a tendency to mistake them for twinning, but Andrade pointed out that their gradual appearance, their distribution, and their noncrystallographic boundaries did not fit this explanation. The observations did indicate that zinc and certain other metals, at least, will, under the proper conditions, bend sharply in some manner about axes in the slip planes, and this appeared to be a possible mechanism for the formation of the striations of fig. 4.

Specimens were cleaved from large single-crystal rods of zinc with round or square cross-sections and were squeezed in a small vise in various crystallographic directions. Squeezing in or near a [100] direction (perpendicular to a second-order prism face) caused a second-order rumpling of the basal cleavage face. (If the tablet was circular, the re-

stress, rather than a first-order rumpling. This was shown in fig. 2. Evidently the crystal rumpled much more easily about a [210] direction than about a [100] direction, at least at room temperature. (Smialowsky<sup>24</sup> found that the stresses for compression perpendicular to second-order prism faces were considerably lower than those for basal or first-order prism faces.) The similarity between



Fig. 4—Deformation markings on cleavage face of deformed single crystal of zinc.

these rumplings and the striations of fig. 4 will be noted.

With continued squeezing, rumpling became more and more exaggerated and eventually the specimens began to buckle. In specimens squeezed in a direction almost perpendicular to second-order prism planes, the buckling or bending occurred generally about second-order traces in the basal plane. In specimens squeezed in a direction almost perpendicular to first-order prism planes, the buckling was more irregular but might have been the resultant of various second-order bucklings. Examples of buckling are pictured in figs. 5 and 6. It is easy to imagine buckling (or, on a smaller scale, rumpling) to result from, or in the formation of, various combinations of bend planes of the type found by Miller. Fig. 7 shows a few such combinations that might account for many of the structures observed. Cleavages through buckled specimens showed that the basal planes did follow essentially the directions indicated.

As far back as 1898, Mügge<sup>25</sup> observed a similar phenomenon in crystals of cyanite compressed parallel to their glide planes. Recently Orowan<sup>26</sup> rediscovered the phenomenon in single crystals of cadmium, as did the present author in zinc. More recently, Hess and Barrett<sup>27</sup> have performed experiments similar to those of Orowan but with small single-crystal rods of zinc. They have observed the same phenomenon and subjected it to a searching analysis. Orowan called this phenomenon "kinking" and considered it (along with slip and twinning) as a third fundamental mechanism of deformation. He, too, rationalized the mechanism in terms consistent with Miller's<sup>19,21</sup> observations of bend planes in zinc and wrote that "deformation bands in metals hith-

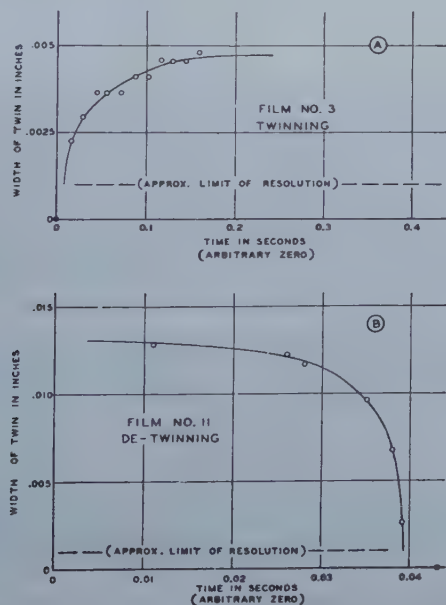


Fig. 3—Analysis of twinning and de-twinning. A. Initial stage of twinning. B. Final stage of de-twinning.

sultant [210] tensile stress caused (102) twinning as well.) This was shown in fig. 1. Squeezing in or near a [210] direction (perpendicular to a first-order prism face) generally caused two sets of second-order rumpling, one on each side of the applied



very much closer together could not be measured. Spots or streaks from other specimens showed lines in two or three directions, presumably from bendings about more than one  $[210]$  direction, or perhaps, remembering the first-order striations of fig. 4, from bendings about  $[100]$  directions as well. Guinier's method<sup>29</sup> should magnify these fine structures and afford an opportunity for closer study. It appears, at present, that rumpling and buckling can consist of large, sharp bends or many fine, slight, close-together bends, or combinations of these and intermediate bendings.

Several investigators<sup>16-18,30</sup> have observed first-order twins and second-order striations on an indented basal cleavage face. In the present work, it was observed that if a  $\frac{1}{2}$ -in. steel ball was dropped about 12 in. onto a basal cleavage face it frequently caused small surface twins at  $60^\circ$  to each other and it made a depression surrounded by second-order striations. It was also observed that a marked, although slight, bulge or mound appeared on the cleavage face on the opposite side of the specimen and that its boundaries were of a second-order hexagonal nature. Subsequent intermediate cleavages showed that each basal plane had a corresponding depression, so that the deformation was evidently in the nature of a bending of the basal planes around  $[210]$  directions rather than any sort of prismatic or pyramidal slip. First-order twinning was limited to areas very near to the surface, but this second-order bending proceeded easily through relatively great distances and, regardless of the direction of the stress applied, the deformation always proceeded in a direction perpendicular to the basal plane. It spread out somewhat, but the boundary or bend plane followed no definite crystallographic direction.

When the impression encountered a bend plane or a grain boundary, it passed through it, with some loss in magnitude (particularly at a grain boundary), and continued in the new crystal in a direction

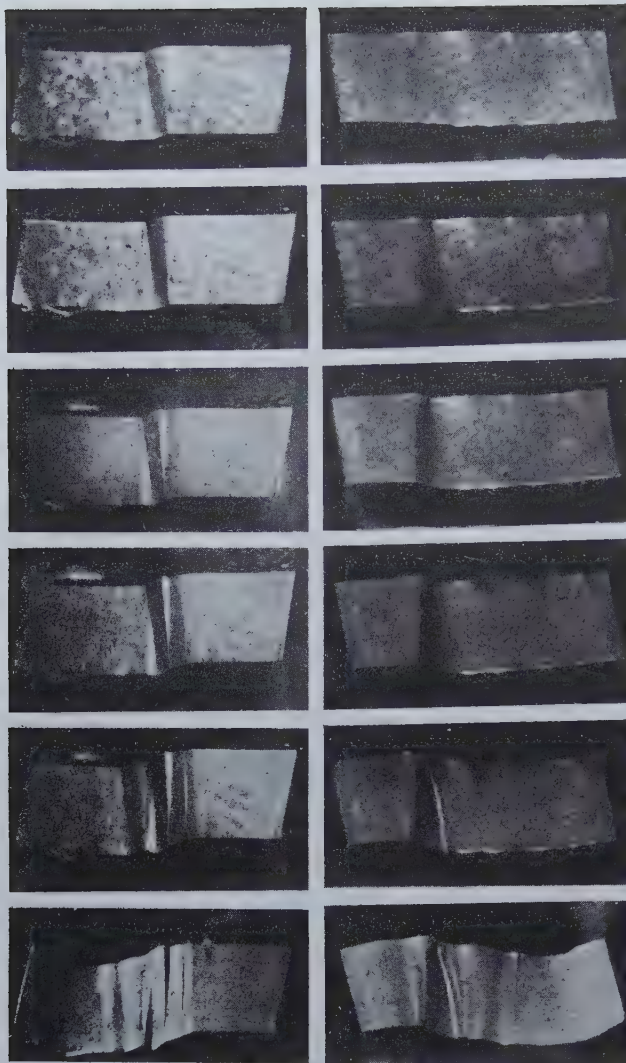


Fig. 5—Steps in buckling of zinc single crystal under compression almost  $\perp (110)$ .

Plane of picture near  $(100)$ . Basal planes horizontal and  $\perp$  plane of picture. Left column, one side of specimen; right column, opposite side of specimen.

erto considered glide or twin bands may be, in reality, kink bands, and the possibility must be kept in mind that glide may begin in many or in all cases with kinking. Further deformation may take place either by glide across the band or by displacement of the planes of kinking representing its boundaries," as observed in cadmium crystals and as postulated by Sir Lawrence Bragg<sup>28</sup> in 1940. Hess and Barrett considered that the structure and formation of kink bands could be accounted for by accepted mechanisms (slip and bend-gliding) and presented a rationalization in terms of dislocation theory.

X-ray back-reflection Laue studies conducted by the present investigator with varying degrees of rumpling, bending, buckling, etc., have shown the development of a fine structure in the Laue spots or streaks consistent with the general ideas developed above. Where bending seemed to have been entirely about a single  $[210]$  direction, the spots appeared to break up into a series of fine parallel lines, in the proper direction, sometimes so close together as to give an essentially continuous streak. Some of the more pronounced lines were measured and found to be of the order of 10 to 40 min apart. Others

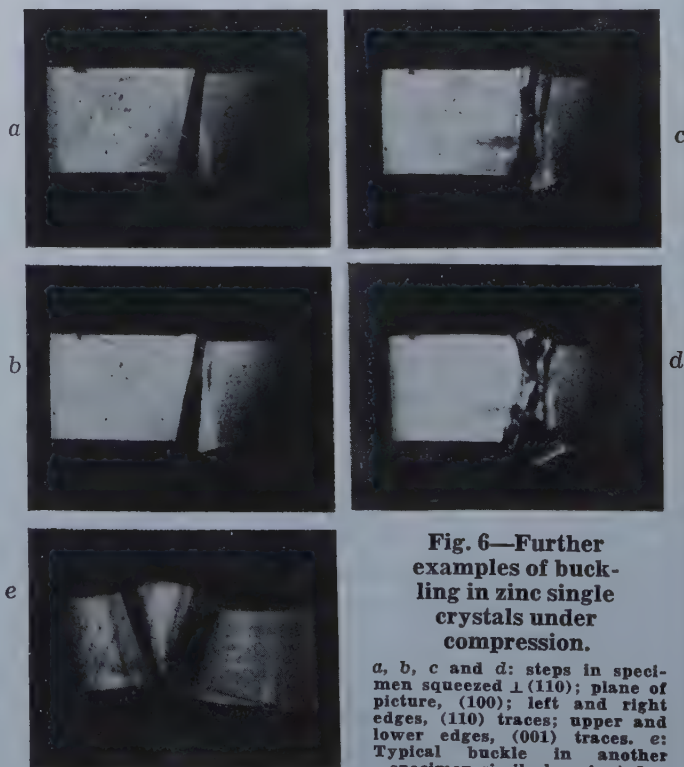


Fig. 6—Further examples of buckling in zinc single crystals under compression.

a, b, c and d: steps in specimen squeezed  $\perp (110)$ ; plane of picture,  $(100)$ ; left and right edges,  $(110)$  traces; upper and lower edges,  $(001)$  traces. e: Typical buckle in another specimen similarly oriented.





Fig. 7—Relation of bend planes to buckling of zinc single crystals.

perpendicular to its basal plane as shown diagrammatically in fig. 8. When the impression encountered a small (102) twin, it apparently de-twinning it, as might be expected, and proceeded on through the crystal as if the twin had not been there. The de-twinning operation, of course, absorbed some energy, and the impression was smaller than it would otherwise have been. Fig. 9 shows two impressions, one going through a twin and one not going through a twin. Careful measurements showed no change in the distance between the markings on the two cleavage surfaces. Had the impression going through the twin not de-twinning it, it should have been offset in passing through the twin and the distance between the mounds on the bottom cleavage should have been measurably smaller than the distance between the impressions on the top cleavage.

A few studies were made of the effects of certain other variables on the nature of indentation deformation. In the specimen of fig. 10, some attention was given to the effect of previous cold work. An impression (the largest) was made, in the manner described above, in the specimen "as cleaved." Then it was squeezed slightly in a [100] direction and another impression was made next to the first. After further slight squeezing, a third impression was made. Top and bottom surfaces were then photographed, as shown at the left. Following this, the specimen was again squeezed slightly (this time causing some twinning) and a fourth impression was made (in an area free of twins). The specimen was again photographed, as shown at the right. As the degree of prior rumpling increased, the second-order bendings or striations around the impression became less noticeable, and, more obviously, the mounds became smaller and sharper and appeared as more perfect, truncated, second-order pyramids.

In the specimen of fig. 11, three impressions were made by dropping the same ball from the same height onto the specimen at three different temperatures. The second-order bendings or striations around the impression became less noticeable as the temperature of test was increased, and the width and hexagonal character of the mound decreased.

Methods of testing the effect of variations in speed of deformation have not yet been well developed, but it seems safe to say, on the basis of the few tests performed, that it may have a very marked effect, particularly when very slow rates are compared with impact rates.

Indentation tests, then, appear to offer a relatively simple and easy way to study qualitatively, if not quantitatively, the effects of variables on the nature of the bending mechanism in zinc single crystals.

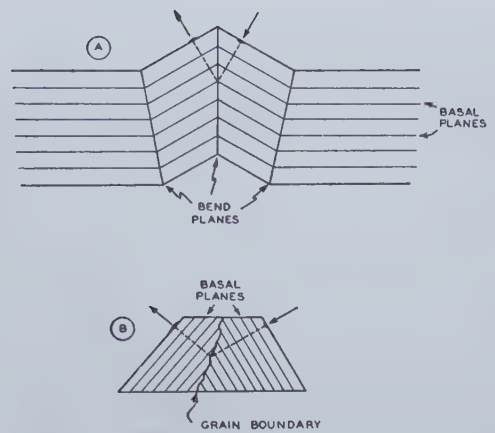


Fig. 8—Passage of a ball impression.

A. Through a bend plane. B. Through a grain boundary.

Temperature, speed, and prior deformation have definite effects.

N.B.: Extraneous crystals in an intended single-crystal specimen can, like indentations, propagate deformations perpendicular to the basal plane for great distances, presumably because of anisotropy of thermal contraction. Care should be exercised in planning critical experiments to assure a source of truly single, undeformed crystals.

One more classification of deformation markings involving bending of the basal planes (and sometimes slip) will be termed accommodation markings. When a (102) twin is formed, a relative shift

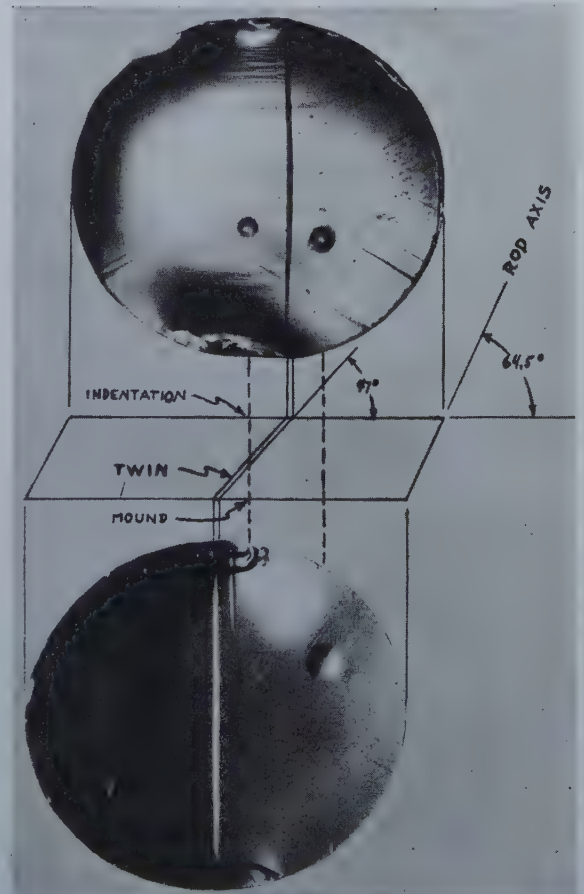
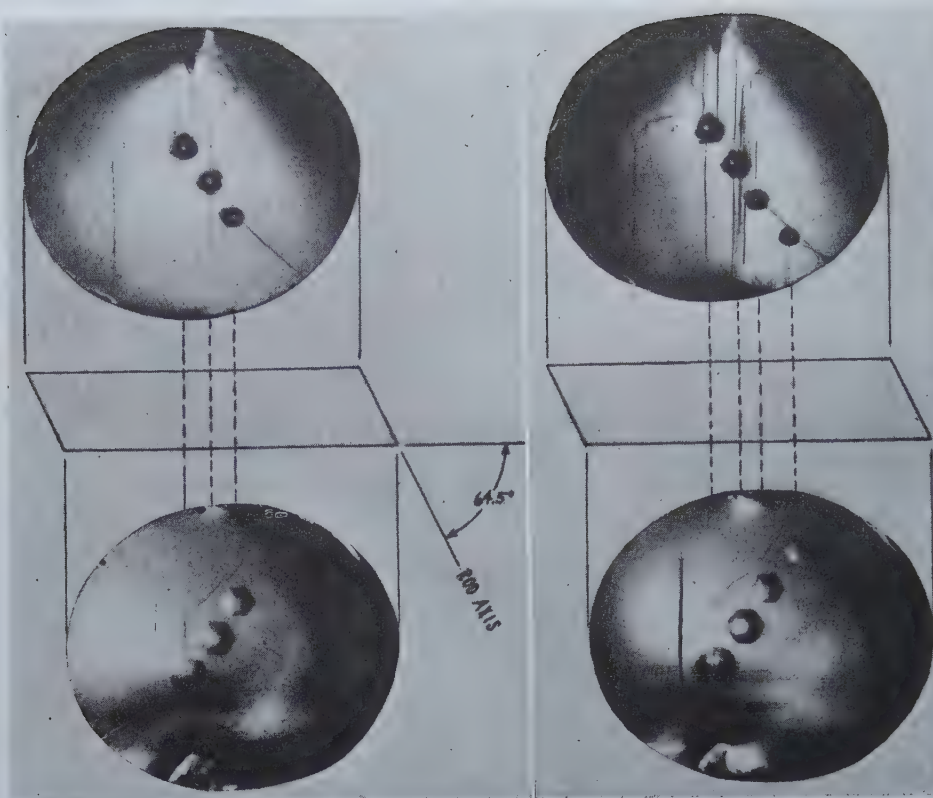


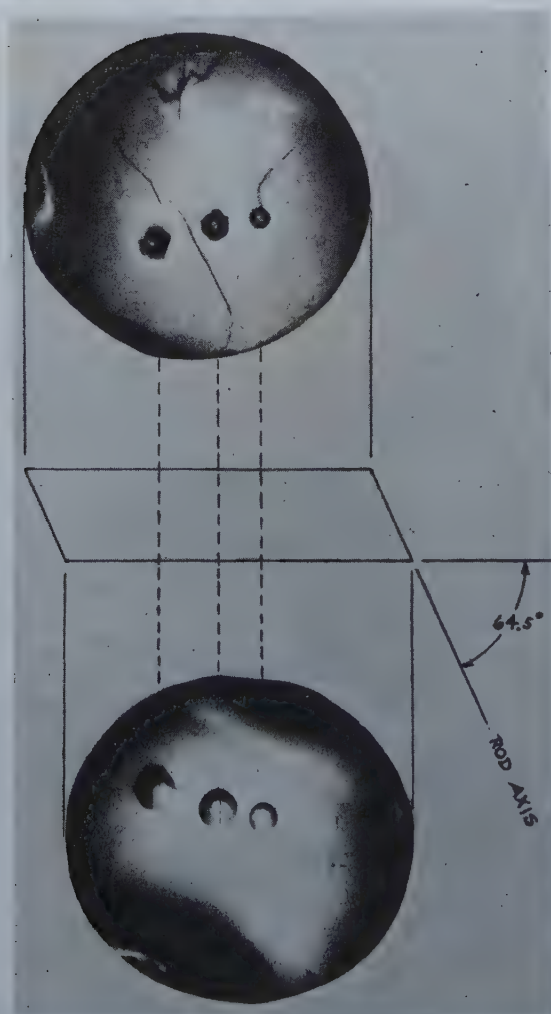
Fig. 9—Effect of a small (102) twin on deformation due to an impact ball impression in the basal plane of a single crystal of 99.99+ pct zinc.





**Fig. 10—Effect of increasing prior deformation on deformation due to an impact ball impression in the basal plane of a single crystal of 99.99+ pct zinc.**

Impression No. 1, least prior deformation, at left. Impression No. 4, greatest prior deformation, at right.



**Fig. 11—Effect of temperature on deformation due to an impact ball impression in the basal plane of a single crystal of 99.99+ pct zinc.**

Left,  $-50^{\circ}\text{C}$ ; center, room temperature; right,  $300^{\circ}\text{C}$ .

in the parts of the parent lattice on each side of the twin is required to accommodate it. If the twin does not go all the way through the crystal, or if it encounters a boundary or barrier of some kind, the shifting of the parent lattice is restricted, and it is frequently observed that the accommodation is accomplished either by bending or by restricted slip. Fig. 12 suggests ways in which this might be accomplished. All of these have been observed, but they have not been studied thoroughly. The bends formed adjacent to a twin appear to be about a  $[100]$  direction, and here, as in one set of the striations in fig. 4, it is presumably a case of first-order bending. Apparent first-order bending is less prevalent than second-order bending, and presumably more difficult (at least at room temperature), but it appears to occur when conditions warrant it. Perhaps it could be rationalized as the resultant of two simultaneous second-order bends.

Accommodation bending of some kind has also been observed adjacent to a long straight boundary between two large grains, as shown in fig. 13. This may be required by differences in thermal contraction. It has not been investigated further.

#### Deformation by Torsion

Only one type of test involving torsion was performed. A cylindrical single-crystal rod having its basal plane essentially perpendicular to the rod axis was twisted about the rod axis. The ease of twisting was startling. No slip markings were observed, and no twinning was noted until a considerable twist had been executed. No simple rationalization of the deformation in terms of slip in the basal plane in close-packed directions was readily pictured. With an undeformed specimen, light etching with 50-50 HCl brought out bright reflections from first-order zones parallel to the rod axis, but with a twisted specimen these reflections spiraled around it. The impression obtained was that the individual



basal planes or very thin packets of basal planes had simply rotated upon each other about the trigonal (specimen) axis without regard for crystallographic requirements. Basal cleavage faces of twisted specimens showed no clear markings that could not have been caused by the cleavage operation. Back-reflection X-ray Laue patterns from these surfaces and from the cylindrical sides of twisted specimens seemed to affirm the gradual change in orientation suggested by the etching experiments. The orientation indicated by the pattern obtained at any particular point along the rod axis was consistent with the degree of twist. A fine structure in the Laue spots may have been due to extraneous deformation, but more careful experiments might yield valuable information.

Collins and Mathewson<sup>31</sup> and Heidenreich and Shockley<sup>32</sup> have reported apparent slight rotations of slip planes of aluminum upon each other about axes perpendicular to those slip planes, but it is difficult to believe that such rotations could occur on the scale and with the ease suggested by the present experiment. Some additional work has been performed, but the results, so far, are inconclusive.

An alternative possibility is that rumpling of the basal planes somehow enters into the picture and affords a mechanism for the deformation observed. For instance, the slight rotations about an axis perpendicular to the slip plane observed by Collins and Mathewson and by Heidenreich and Shockley might have been caused by rumpling about other directions in addition to that perpendicular to the slip direction. The idea that rumpling may play a part in torsional deformation is certainly suggested by results obtained by Gough and Cox<sup>15</sup> when they subjected a single crystal of zinc, with the basal plane  $15^\circ$  removed from the critical orientation under discussion, to alternating torsional stresses. The fractured specimen showed macroscopic rumpling or buckling of the basal plane. No such rumpling, even on a microscopic scale, was definitely observed, however, in the present work. It might be mentioned also that annealing at  $400^\circ\text{C}$  caused no obvious change in a twisted specimen, or in its Laue pattern, provided the twisting had not been severe enough to cause twinning.

### Cleavage

Very many cleavages were performed, in the course of the present investigations, in many different ways and under many different conditions. At no time was a cleavage observed that could definitely be identified as anything other than a basal cleavage. In no case was a "perfect" cleavage surface obtained. The best surface was obtained by slow pulling of a specimen with the basal plane almost perpendicular to the rod axis under conditions of nearly perfect axiality. Any departure from these conditions that increased extraneous deformation gave less perfect cleavages.

A recent publication by Zapffe<sup>30</sup> described some of the features of basal cleavages of zinc crystals. The markings he described as "fissures" must have been tear lines, where the cleavage passed from one basal plane to another of the original crystal by cleaving through the basal planes of small twins formed by the tearing. The "secondary cleavages" he showed must have been in twins formed prior to cleaving and were probably basal cleavages through

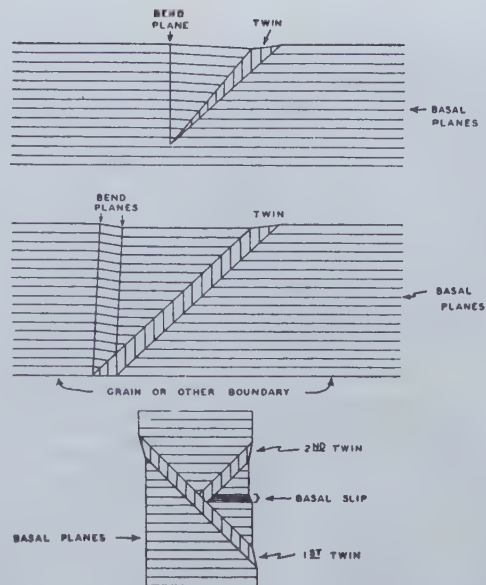


Fig. 12—"Accommodation" of (102) twins by bending or basal slip.

the twins and de-twinning or re-twinning portions of those twins. Zapffe failed to establish any other identity for these cleavages.

It was noted that there was a distinct tendency for specimens lightly etched with 50-50 HCl to hold together at the surface even when cleavages through the bodies of the specimens were otherwise quite complete. Greenland<sup>22,33</sup> noted the same tendency with single crystals of mercury. It is not known what the effect of a change in surface preparation would be.

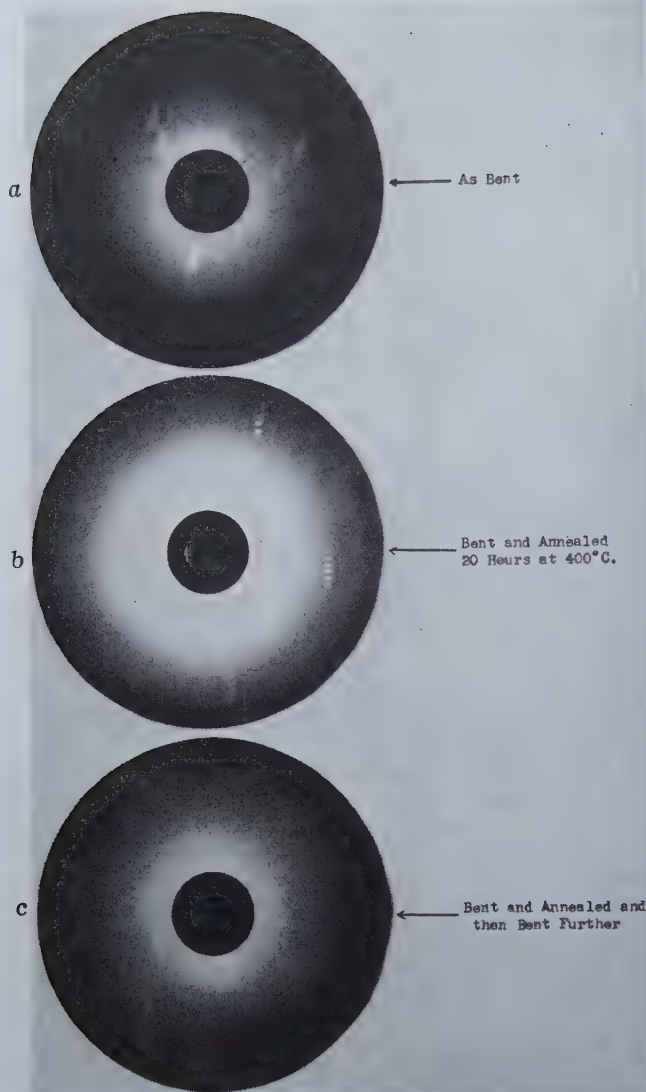
### Annealing Effects

No systematic study of annealing effects was planned as part of the present work, but some of the specimens were annealed, usually at  $400^\circ\text{C}$  for 20 to 48 hr, sometimes for shorter periods, and then were examined. Others were examined after long periods at room temperature.



Fig. 13—"Accommodation" bending (dark band) at a grain boundary (right edge of band).





**Fig. 14—Effect of bending and annealing of single crystals of 99.999+ pct zinc on the fine structure of Laue spots.**

a. As bent. b. Bent and annealed 20 hr at 400°C. c. Bent and annealed and bent further.

Single crystal specimens of  $\frac{1}{2}$  in. diam bent about 1 in. radii, stretched up to 25 pct, or twisted as much as 35° per inch of length, at room temperature and *without twinning*, and subsequently annealed at 400°C or aged at room temperature, showed no evidence, upon etching or upon X-ray back-reflection Laue examination, of any recrystallization. Annealing may have influenced the fine structure of the Laue spots, but apparently such specimens contained no nuclei for the formation of new grains. Recrystallization occurred readily in specimens containing crossed twins, and new crystals were actually observed at the points where twins had met or crossed. Thin, single, uncrossed twins frequently appeared to be reabsorbed by the parent lattice, while thicker ones appeared to be unaffected. These observations are, in general, consistent with the findings of Mathewson and Phillips,<sup>9</sup> Kuznetsov and Zolotov,<sup>34</sup> and others.<sup>24,35</sup> Kuznetsov and Karpova<sup>36</sup> reported finding new grains at all twins if the annealing conditions were correct.

In the few cases investigated in the present work, the orientation of a new grain did not correspond closely with that of a twin or that of the parent lattice, in disagreement with Miller<sup>37</sup> and lending credence to the idea of the Russian investigators<sup>38,39-40</sup> that the twin itself is not the nucleus. However, the present results do not necessarily support their contention that the nucleus is in the twin boundary. If the nucleus were to lie in the area where twins meet or cross, it might not have the orientation of either of the twins, or of the matrix. Speculation is aroused as to whether crossed deformations of other types, such as crossed bucklings or rumpings or bend planes, or crossings of these with each other or with twins, might generate areas in which, under the proper conditions, nuclei could germinate. Zinc, with only one slip plane, does not, perhaps, offer so many opportunities for this to occur, and zinc therefore may depend more largely upon crossed twinning for the generation of recrystallization nuclei than do certain other metals.

Another annealing effect of interest was the apparent ability of supposedly undeformed single crystals of zinc to reorient through angles as high as 35° without undergoing recrystallization—that is, without the formation of a new crystal which grows and eventually absorbs all of the old one. This was first noted in this laboratory a few years ago by G. Edmunds, who annealed a large single crystal, prepared by the usual Bridgman method, at a temperature near the melting point and found that the basal cleavage, relatively perfect in each case, had shifted through an angle of about 30°. In the present work, this has never been observed in specimens of a high original degree of perfection, but it has been observed several times in specimens known to contain slight imperfections such as bandings that might have resulted from deformation during growth and cooling or from subsequent handling. It might be supposed that one of these bands simply absorbed the rest of the crystal, but in cases where these bands differed by a very few degrees, the final change in orientation was sometimes of the order of 25° to 35°. Kronberg and Wilson<sup>41</sup> have evolved a formal relationship between pairs of orientations which may explain extensive apparent rotations of a structure in terms of small atomic movements. Whether such a mechanism could be applied here is not known, but it might be given consideration.

One more annealing effect will be mentioned. It was found that if single-crystal specimens of 99.999+ pct zinc were bent and cleaved, the basal cleavage surface was not a perfectly smooth curve but contained a very large number of very small facets probably due primarily to second-order bends about axes perpendicular to the slip direction. When such a specimen was annealed for 20 hr at 400°C before cleaving, some of the facets apparently grew at the expense of their neighbors and became quite obvious to the unaided eye. Fig. 14 shows back-reflection Laue X-ray patterns from a bent cleavage surface “as bent” and after subsequent annealing. The fine structures are consistent with the visual observations. Further bending, after annealing, broke up these facets again into smaller facets, and the fine structure of the Laue spots was similar to that of the unannealed specimen, as shown in the third print of fig. 14. Guinier and his



coworkers<sup>1,20</sup> have observed a similar effect, on a more microscopic scale, in aluminum, and Cahn<sup>42</sup> has reported similar results with high purity zinc. The distinguishing feature of the present work was that the phenomenon could be observed readily without resort to microscopic or X-ray methods of examination and that it indicated that the "polygonization" of the structure, as Guinier has termed it, was not *caused* by the annealing but merely rendered more macroscopic thereby, and hence more easily detectable.

### General Discussion of Results

The phenomena involving bending of the "slip" plane seem to be of particular significance. In the present work, many manifestations of the ease and likely importance of this mechanism in zinc have been observed. Influences of the temperature and speed of deformation and of the prior state of deformation have been clearly indicated. Similar phenomena have been observed in Cd,<sup>28</sup> Mg,<sup>43</sup> Be,<sup>44</sup> Na,<sup>28</sup> Al,<sup>81</sup> and probably many other metals. The exact mechanism has not been established, but the author independently arrived at premises essentially consistent with those advanced by Orowan<sup>28</sup> and, more recently, by Hess and Barrett.<sup>87</sup> These premises seem consistent also with experimental and, in some cases, theoretical observations of other workers and on other metals.

Orowan classed bending or kinking, along with slip and twinning, as one of the three fundamental mechanisms of deformation in metals. The present author is inclined to suggest that this phenomenon, manifested in bending, rumpling, buckling or kinking, and probably in other forms, may be the essential difference between the apparently homogeneous shear of twinning and the inhomogeneous shear observed in gliding or slip processes. It would seem capable of supplying a mechanism for the generation of the discontinuities of current dislocation theories of slip. In other words, bendings of the slip plane may be the more fundamental phenomenon, and inhomogeneous shearing of slip may be merely a consequence. Many investigations, including recent work by the author,<sup>†</sup> have failed to show

<sup>†</sup> Reported in a paper by D. C. Jillson: Quantitative Stress-Strain Studies on Zinc Single Crystals in Tension. To be published in *Trans. AIME* 188, *Jnl. of Met.* 1950, TP 2899E.

any influence of variations in the component of stress normal to the slip plane upon the critical value of the component along the slip plane in the slip direction required to initiate slip. But if bending or rumpling of the slip plane, on a microscopic or submicroscopic scale, occurs before the normal component attains a readily measurable value, and hence supplies a mechanism for slip with only the slightest normal component, it would seem entirely consistent that variations in the normal component above this slightest value would not affect the critical resolved stress for the initiation of slip. On the other hand, twinning appears to occur by homogeneous shear along the twinning plane without any rumpling of the twinning plane. This process, then, might be expected to be affected by variations in the normal component, and such an effect has been reported by several investigators.<sup>14,15,10,45</sup> Rumpling on a macroscopic scale is easily demonstrated. It is not difficult to believe that it can occur also on a microscopic or submicroscopic scale. The asterism of Laue spots can perhaps be explained as well by

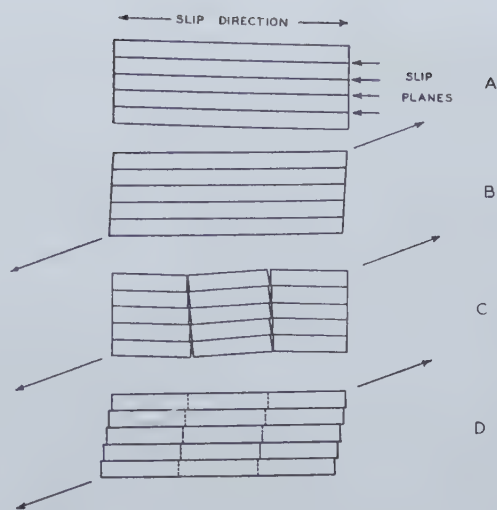


Fig. 15—Suggested relation of rumpling to slip.

a rumpling mechanism as by any other.<sup>81, 43, 46-50</sup> The development of improved methods for studying the fine structure of Laue spots may permit a definite answer to this question.

The mechanism pictured by the author is represented very simply in fig. 15. Step A represents the perfect, undistorted lattice. The lines probably indicate blocks of planes rather than individual planes. Step B suggests slight elastic deformation resulting from an applied stress as indicated. (All of the steps are greatly exaggerated.) Step C suggests a breaking up or bending or rumpling of the lattice about axes in the slip plane perpendicular to the slip direction, relieving the elastic strain at least partially. This probably involves restricted glide in a portion of the lattice as shown. Subsequent steps might be viewed in various ways. The lattice might tend to heal by further restricted glide, as suggested in step D, and a rapid or continuous succession of rumplings and healings would result in a more or less continuous glide until complications such as rumplings in other directions interfered with the process and brought it to a halt, at least temporarily. Alternatively, the bend planes which bound the rumple might be considered to move in the manner suggested by Bragg.<sup>88</sup> Still again, the discontinuities generated by the rumpling might be viewed as dislocations, which indeed they are, and considered to diffuse or travel through the lattice in the manner of dislocation theory. Perhaps there is no great basic difference between these different views.

It has been demonstrated macroscopically in the present work that bending or rumpling occurs with great ease and that a bend or rumple in a given slip plane or block of slip planes is propagated with great ease and rapidly in directions normal to this plane for considerable distances before being extinguished, the magnitude of the lattice faults formed probably decreasing with the distance. It has also been indicated that variations in temperature, rate of deformation, and other factors affect the magnitude and spacing of the bends. It would seem that here may be a means of explaining many of the observed phenomena of deformation, such as the jumps noted in precise stress-strain determinations, the spacing of slip planes, strain hardening, etc., and that it may supply a precise mechanistic picture for dislocation theories.



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# Discussion—Institute of Metals Division\*

## Cleveland Meeting, October 1949

The Origin of Annealing Twins in Brass (paper by R. Maddin, C. H. Mathewson, and W. R. Hibbard, Jr. <i>Jnl. Met.</i> Sept. 1949, TP 2676E).....	1020
Annealing Twins in Copper and 70-30 Alpha Brass (paper by W. R. Hibbard, Jr., Y. C. Liu, and S. F. Reiter. <i>Jnl. Met.</i> Sept. 1949, TP 2677E).....	1020
Structure and Nature of Kink Bands in Zinc (paper by J. B. Hess and C. S. Barrett. <i>Jnl. Met.</i> Sept. 1949, TP 2688E).....	1022
The Vapor Pressures of Zinc and Cadmium over Some of Their Silver Alloys (paper by C. E. Birchenall and C. H. Cheng. <i>Jnl. Met.</i> July 1949, TP 2601E).....	1022
The Diffusion and Solubility of Carbon in Alpha Iron (paper by J. K. Stanley. <i>Jnl. Met.</i> Oct. 1949, TP 2679E).....	1023
Analysis of Interstitial Diffusion Using Activity Methods (paper by A. G. Guy. <i>Jnl. Met.</i> Sept. 1949, TP 2604E).....	1024
The Study of Grain Boundaries with the Electron Microscope (paper by J. F. Radavich. <i>Jnl. Met.</i> July 1949, TP 2623E).....	1026
Studies of Interface Energies in Some Aluminum and Copper Alloys (paper by K. K. Ikeuye and C. S. Smith. <i>Jnl. Met.</i> Oct. 1949, TP 2691E).....	1026
P-type and N-type Silicon and the Formation of the Photovoltaic Barrier in Silicon Ingots (paper by J. H. Scaff, H. C. Theuerer, and E. E. Schumacher. <i>Jnl. Met.</i> June 1949, TP 2586E).....	1027
Microstructures of Silicon Ingots (paper by W. G. Pfann and J. H. Scaff. <i>Jnl. Met.</i> June 1949, TP 2587E).....	1027
Electrical Properties of the Intermetallic Compounds $Mg_2Sn$ and $Mg_2Pb$ (paper by W. D. Robertson and H. H. Uhlig. <i>Met. Tech.</i> Oct. 1948, TP 2468E).....	1028
Ferromagnetic Alloys in the Systems Cu-Mn-In and Cu-Mn-Ga (paper by F. A. Hames and D. S. Eppelsheimer. <i>Jnl. Met.</i> Aug. 1949, TP 2600E).....	1028
The Beryllium-iron System (paper by R. J. Teitel and M. Cohen. <i>Jnl. Met.</i> April 1949, TP 2550E).....	1028
Solubility of Titanium in Liquid Magnesium (paper by K. T. Aust and L. M. Pidgeon. <i>Jnl. Met.</i> Sept. 1949, TP 2680E).....	1029
Liquid Solubility of Manganese in a Magnesium-aluminum-tin Alloy (paper by B. J. Nelson and G. F. Sager. <i>Jnl. Met.</i> July 1949, TP 2602E).....	1029
A Metallographic Description of Fracture in Impact Specimens of a Structural Steel (paper by M. Baeyerztz, W. F. Craig, Jr., and E. S. Bumps. <i>Jnl. Met.</i> Aug. 1949, TP 2635E).....	1030
The Effect of Ferrite Grain Size on Notch Toughness (paper by J. M. Hodge, R. D. Manning, and H. M. Reichhold. <i>Jnl. Met.</i> March 1949, TP 2553E).....	1033
Investigation of Temper Brittleness in Low-alloy Steels (paper by S. A. Herres and A. R. Elsea. <i>Jnl. Met.</i> June 1949, TP 2574E).....	1034
The Effects of Molybdenum and Commercial Ranges of Phosphorus upon the Toughness of 0.40 Pct Carbon Chromium Steels (paper by M. Baeyerztz, W. F. Craig, Jr., and J. P. Sheehan. <i>Jnl. Met.</i> Aug. 1949, TP 2654E).....	1035
Discontinuous Crack Propagation—Further Studies (paper by L. D. Jaffe, E. L. Reed, and H. C. Mann. <i>Jnl. Met.</i> Oct. 1949, TP 2682E).....	1035
Stress and Strain States in Elliptical Bulges (paper by C. C. Chow, A. W. Dana, and G. Sachs. <i>Jnl. Met.</i> Jan. 1949, TP 2485E).....	1036
The Comparative Creep Properties of Several Types of Commercial Coppers (paper by A. D. Schwoppe, K. F. Smith, and L. R. Jackson. <i>Jnl. Met.</i> July 1939, TP 2605E).....	1037
The Active Slip Systems in the Simple Axial Extension of Single Crystalline Alpha Brass (paper by R. Maddin, C. H. Mathewson, and W. R. Hibbard, Jr. <i>Jnl. Met.</i> Aug. 1949, TP 2658E).....	1037
Simultaneous Aging and Deformation in Metals (paper by J. D. Lubahn. <i>Jnl. Met.</i> Oct. 1949, TP 2697E).....	1038
The Transverse Bending of Single Crystals of Aluminum (paper by M. K. Yen and W. R. Hibbard, Jr. <i>Jnl. Met.</i> Oct. 1949, TP 2687E).....	1038
Stages in the Deformation of Monel Metal as Shown by Polarized Light (paper by D. H. Woodard. <i>Jnl. Met.</i> Oct. 1949, TP 2696E).....	1041
Influence of Temperature on the Stress-strain-energy Relationship for Copper and Nickel-copper Alloy (paper by D. J. McAdam, Jr. <i>Jnl. Met.</i> Oct. 1949, TP 2703E).....	1042
A Method of Examination of Sections of Fine Metal Powder Particles with the Electron Microscope (paper by L. Delisle. <i>Jnl. Met.</i> March 1949, TP 2538E).....	1045
Determination of Boundary Stresses during the Compression of Cylindrical Powder Compacts (paper by M. E. Shank and J. Wulff. <i>Jnl. Met.</i> Sept. 1949, TP 2678E).....	1045
A Dilatometric Study of the Sintering of Metal Powder Compacts (paper by P. Duwez and H. Martens. <i>Jnl. Met.</i> Sept. 1949, TP 2673E).....	1046
Electrical Resistivity Measurements on Iron-silicon Compacts Prepared by the Powder Metallurgy Procedure (paper by F. W. Glaser. <i>Jnl. Met.</i> Aug. 1949, TP 2660E).....	1048
The Yielding and Strain-aging of Carburized and Nitrided Single Crystals of Iron (paper by H. Schwartzbart and J. R. Low, Jr. <i>Jnl. Met.</i> Sept. 1949, TP 2603E).....	1049

\* TP 2908E.



Size Effects in Quenching High-purity, Precipitation-hardenable Alloys (paper by W. L. Finlay. <i>Jnl. Met.</i> Oct. 1949, TP 2694E).....	1050
Secondary Recrystallization in Copper (paper by M. L. Kronberg and F. H. Wilson. <i>Jnl. Met.</i> Aug. 1949, TP 2634E).....	1050
Recovery and Recrystallization in Brass (paper by B. L. Averbach. <i>Jnl. Met.</i> Aug. 1949, TP 2636E).....	1057
Recrystallization Texture and Coarsening Texture in High Purity Aluminum (paper by P. A. Beck and H. Hu. <i>Jnl. Met.</i> Sept. 1949, TP 2675E).....	1057
Recrystallization and Microstructure of Aluminum Killed Deep Drawing Steel (paper by R. L. Rickett, S. H. Kalin, and J. T. MacKenzie, Jr. <i>Jnl. Met.</i> March 1949, TP 2552E).....	1059
The Crystal Structure of Ni <sub>3</sub> W (paper by E. Epremian and D. Harker. <i>Jnl. Met.</i> April 1949, TP 2551E).....	1060
Structure of Diborides of Titanium, Zirconium, Columbium and Vanadium (paper by J. T. Norton, H. Blumenthal, and S. J. Sindeband. <i>Jnl. Met.</i> Oct. 1949, TP 2689E).....	1060
The Isolation of Carbides from High Speed Steel (paper by D. J. Blickwede and M. Cohen. <i>Jnl. Met.</i> Sept. 1949, TP 2625E).....	1061
Oriented Arrangements of Thin Aluminum Films on Ionic Substrates (paper by T. N. Rhodin, Jr. <i>Jnl. Met.</i> June 1949, TP 2575E).....	1062
Kinetics of the Reactions of Zirconium with O <sub>2</sub> , N <sub>2</sub> , and H <sub>2</sub> (paper by E. A. Gulbransen and K. F. Andrew. <i>Jnl. Met.</i> Aug. 1949, TP 2659E).....	1062
Kinetics of the Reactions of Titanium with O <sub>2</sub> , N <sub>2</sub> , and H <sub>2</sub> (paper by E. A. Gulbransen and K. F. Andrew. <i>Jnl. Met.</i> Oct. 1949, TP 2684E).....	1063
The Lattice Parameters of High Purity Alpha Titanium; and the Effects of Oxygen and Nitrogen on Them (paper by H. T. Clark, Jr. <i>Jnl. Met.</i> Sept. 1949, TP 2656E).....	1064
The Effect of Oxygen, Nitrogen, and Hydrogen on Iodide Refined Titanium (paper by R. I. Jaffee and I. E. Campbell. <i>Jnl. Met.</i> Sept. 1949, TP 2681E).....	1064
Preparation and Casting of Beryllium Melts (paper by J. G. Kura, J. H. Jackson, M. C. Udy, and L. W. Eastwood. <i>Jnl. Met.</i> Oct. 1949, TP 2701E).....	1065
Metallographic Examination of Beryllium Alloys (paper by M. C. Udy, G. K. Manning, and L. W. Eastwood. <i>Jnl. Met.</i> Oct. 1949, TP 2700E).....	1065
Kinetics of the Austenite→Martensite Transformation (paper by J. C. Fisher, J. H. Hollomon, and D. Turnbull. <i>Jnl. Met.</i> Oct. 1949, TP 2674E).....	1065
The Free Energy Change Accompanying the Martensite Transformation in Steel (paper by J. C. Fisher. <i>Jnl. Met.</i> Oct. 1949, TP 2704E).....	1066
The Transformation in $\beta$ -CuAl Alloys (paper by E. P. Klier and S. M. Grymko. <i>Jnl. Met.</i> Sept. 1949, TP 2573E).....	1066
Transformation of Gamma to Alpha Manganese (paper by E. V. Potter, H. C. Lukens, and R. W. Huber. <i>Jnl. Met.</i> July 1949, TP 2583E).....	1067

## The Origin of Annealing Twins in Brass

by R. Maddin, C. H. Mathewson, and W. R. Hibbard, Jr.

DISCUSSION, F. H. Wilson presiding

C. S. BARRETT—Is it not likely that along the planes where slip has occurred there is a more complex distortion than the simple shear needed to produce a twin fault? Whatever the conditions along the operative slip plane, they might not only be such as to originate an annealing twin, as is discussed in this paper, but also as to act as a barrier to the growth of a twin. The operative slip plane might act as a barrier by containing material with an orientation that could not be absorbed easily by a growing twin, thus producing a composition plane that is parallel to the operative slip plane.

C. S. BARRETT, *Institute for the Study of Metals, University of Chicago, Chicago, Ill.*

R. MADDIN (author's reply)—With the action of three slip planes and the accompanying rotation of each plane about a different axis, it would seem that the volume surrounding the twin-faulted position is highly distorted as Dr. Barrett points out. Certainly from past investigations of slip lines and the present work, the primary slip planes can be conceived as containing many folds variously distorted by the different rotations of planes which intersect these primary slip planes. Consequently, the position of maximum distortion within the strain volume may be considered to be the nucleus (the twin-faulted position) from which an annealing twin might grow. The highly distorted volume surrounding the twin fault may also be considered to be a barrier which prevents the locked atom from completing the second half of the coordinated  $\langle 112 \rangle$  movements. A cooperative

mechanism for growth (such as the rotation mechanism suggested by Kronberg and Wilson) acting under an activation energy provided by the elevated temperature and driven by the strain energy supplied by the barrier could produce the annealing twin in its observable form.

It would seem, from Dr. Barrett's remarks, that a planar barrier would be required in order to produce a composition plane parallel to the operative slip plane. In view of the complex rotations associated with the movement of slip planes, it is difficult to conceive of a planar barrier.

## Annealing Twins in Copper and 70-30 Alpha Brass

by W. R. Hibbard, Jr., Y. C. Liu, and S. F. Reiter

DISCUSSION, F. H. Wilson presiding

P. A. BECK—It is mentioned in the paper that "the twins coalesce within the grains at higher temperatures." I wonder whether the authors would like to elaborate somewhat on the mechanism by which this process of coalescence is supposed to take place. It is interesting to note in table I, that in copper, where the number of twins per grain was independent of the annealing temperature, little or no increase in grain size was observed with increasing annealing temperature. On the other hand, in brass, where a substantial decrease in the number of twins per grain took place with increasing annealing temperature, there was at the same time a considerable extent of grain growth. It would appear, then, that the structure as recrystallized has the largest number of twins per grain, and that with continued grain growth the number of twins per grain decreases. It seems to me quite likely that



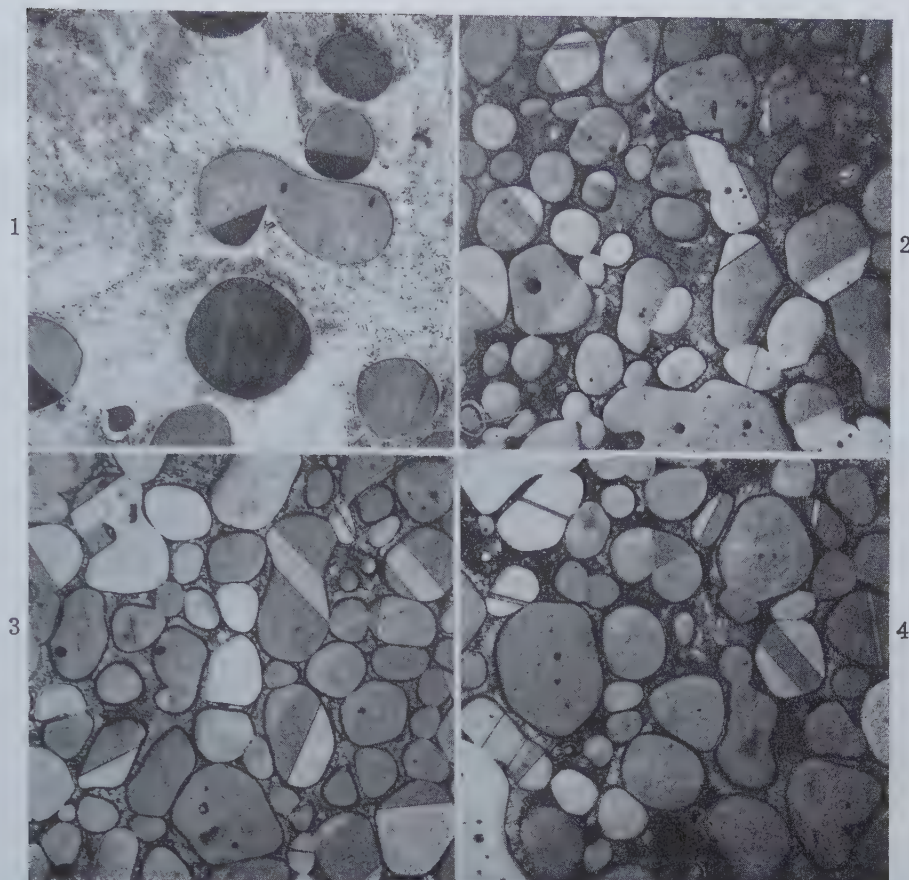
Fig. 1—Copper-silver alloy (45 pct Cu) cold-rolled 50 pct reduction in thickness, annealed 4 hr at 750°C, 1 hr at 800°C and quenched. Dichromate etch. X500.

Fig. 2—Copper-silver alloy (75 pct Cu). Same treatment as fig. 1. X200.

Fig. 3—Same sample as fig. 2, another field. X200.

Fig. 4—Same sample as fig. 2, another field. X250.

Figs. 1-4. Area reduced approximately five ninths in reproduction.



this decrease is not a result of "coalescence," but of the absorption of twins (together with their matrix grains) during the grain growth process at a rate higher than that of the formation of new annealing twins.

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C. S. BARRETT—I have a comment with regard to conclusion No. 3, that "significantly fewer twins were formed at the highest annealing temperature under all rolling conditions." Even though fewer twins were found after the highest temperature anneals, it does not follow necessarily that fewer annealing twins actually had formed during the early stages of annealing. Many that had formed must have been absorbed during growth when grain boundaries swept across them. Comparisons should, therefore, be made only between specimens in which the same amount of grain growth had occurred. In the present experiments the starting grain size was constant, but the final grain size varied from 0.025 to 0.045 mm in copper specimens and from 0.015 to 0.090 mm in brass specimens. Thus the amount of grain growth differed and, therefore, the loss of twins during growth must have differed.

C. S. SMITH—The authors refer to my earlier discussion of spherical grains. It is, of course, impossible to get a spherical grain in a polycrystalline solid, for the contact with boundaries of neighboring grains inevitably produces a multi-edge polyhedron. Nearly spherical grains can, however, be produced if a polycrystalline alloy is partly melted. Figs. 1 to 4 herewith show the microstructure of copper-silver alloys cold-rolled, annealed at 800°C (just above the eutectic temperature), and quenched. Because of the finely dispersed two-phase nature of the alloy, the grain size before melting was small and the grains shown have grown mostly by solution and redeposition through the medium of the liquid phase. The typical grain boundary in the alloy concerned obviously has an

energy greater than twice the crystal-liquid interface, for the dihedral angle is zero, and the liquid has penetrated between the grains, separating them into isolated crystals. Many of the grains are approximately circular in cross-section, and can be assumed to be spheres, though the surface energy evidently does vary slightly with orientation. It is quite obvious that my earlier prediction was wrong, for about half the grains have one or more twins.

There are many grains crossed entirely by twins, in which case the twin boundary joins the surface of the grain with only very slight displacement of the surface. This is in accord with the concept of surface tension equilibrium between the extremely small energy of the twin boundary and that of the interface between the grain (of either exposure) and the liquid. Totally different shapes result, however, when a twin terminates without completely crossing a grain. Since two parts of a grain in twin relation to each other can share only one (111) plane—the twinning plane—any other junction between them must be at a plane along which exact matching of atom positions cannot occur, and hence would be expected to be of higher energy, although for some critical orientations it might be of energy lower than the average randomly oriented interface. On inspecting the micrographs it is apparent that the liquid, in attempting to attain equilibrium, has penetrated into the boundaries at which twins terminate and has produced the sharply re-entrant surfaces shown. If it were possible for the twin boundary to move sideways, no such structure could exist. The twin boundary behaves as if it were anchored in the crystal, and the other surfaces establish surface equilibrium in a geometry exactly analogous to that of a mechanical model in which strings of various tensions are attached to a trolley which may run freely but only along a straight track in a fixed direction. This model—devised by J. C. Fisher and the writer in discussion with J. P. Nielsen\*—will also explain the shape

\* See discussion by Nielsen on page 1026.

of grain boundaries in the vicinity of twin boundaries in solid single-phase metals, and provide for the pres-



ence therein of angles greater than  $180^\circ$ . If the twin boundary energy is zero, the other two boundaries will reach a geometry determined by the equality but opposite signs of their projection in the twinning plane. If the twin is not of zero energy, an additional force, also lined up in the twinning plane, will exist.

If one accepts this—and other—evidence that a twin interface cannot move normal to itself, one must then seek an explanation of the apparent growth of twins as the grains themselves grow in terms of what occurs at the boundary as it advances through adjacent grains of varying sizes and orientations.

In figs. 1 to 4 there are occasional pairs of grains observed with a solid grain boundary between them, and a positive dihedral angle ( $60^\circ$  to  $120^\circ$ ). Such boundaries are invariably straight and probably are boundaries of energy lower than normal, but still much higher than that of twin boundaries, formed between crystals having in common planes of relatively low indexes, perhaps a result of the meeting of two twins from a single primary crystal, which would have in common (114) planes.

W. R. HIBBARD, JR., Y. C. LIU, and S. F. REITER (authors' reply)—Observation 4 in the paper regarding the number of twin-free grains is in error. The ratios of twin-free to total grains are as follows:

Temperature, $^\circ\text{C}$		Twin Free/Total Grains	
Rolling	Annealing	Copper	Brass
—70	400	0.42	0.06
—70	500	0.43	0.06
—70	600	0.32	0.09
25	400	0.42	0.10
25	500	0.33	0.06
25	600	0.34	0.10
200	400	0.39	0.09
200	500	0.37	0.04
200	600	0.36	0.12

Thus, copper has significantly *fewer* (rather than *more* as stated in the paper) twin-free grains for the highest anneal. This trend suggests that twin-containing grains grow at the expense of twin-free grains. (Rather than the reverse as stated in the paper.) There appears to be considerably fewer twin-free grains in brass than in copper, and for the former the ratio appears to be approximately the same for all annealing temperatures, quite different from the trend in copper. Regarding "coalescence," we wonder how a small grain with many thin twins grows to a large grain with twins apparently wider than the original grain size. We agree with Dr. Barrett's comment. The use of "formed" rather than "found" was due to the original hope that the twin/grain ratio would be independent of grain size and the ratio found would also be that formed. Regarding Dr. Smith's comment, we did not intend to imply geometrically spherical grains but rather that if the polyhedral grain has more edges, it may be more stable.

## Structure and Nature of Kink Bands in Zinc

by J. B. Hess and C. S. Barrett

DISCUSSION, G. P. Halliwell presiding

W. R. HIBBARD, JR.—Might the "kinking" mechanism occur in certain suitably oriented grains in polycrystalline zinc during the early stages of rolling to produce deformation bands?

E. A. ANDERSON—I would suggest that Mr. Hess look for deformation bands, because they may be there. A few years ago G. Edmunds published a paper from our laboratory, demonstrating that the preferred form of crystal growth in zinc was with the basal plane in the direction of heat flow. This places it perpendicular to the slab surface, and it is this type of mechanism that seemingly must act at the very start of the rolling operation.

G. EDMUNDS—I am wondering, in line with Mr. Anderson's comment, whether the constraint afforded by the neighboring columnar grains in a polycrystalline specimen would permit the kink band type of deformation.

W. R. HIBBARD, JR., Department of Metallurgy, Yale University, New Haven, Conn.; E. A. ANDERSON, Research Division, The New Jersey Zinc Co., Palmerston, Pa.; G. EDMUNDS, Metallurgical Department, American Brake Shoe Co., Mahwah, N. J.

J. B. HESS and C. S. BARRETT (authors' reply)—Some additional experiments show that kinking occurs even when a crystal is constrained by surrounding material. A single crystal rod from the stock previously used was embedded in a paraffin cylinder and compressed axially. The rod kinked profusely. The length of individual kinks were of the order of one-third the rod diameter, as compared with kink lengths 5 to 7 times the rod diameter that were not unusual in unsupported rods of the same dimensions. Still shorter kinks developed in a rod that was cast into a cylinder of 50-50 solder and then compressed.

Following Mr. Anderson's suggestion, we examined metallographically a cast slab that had been compressed about 5 pct. Several unmistakable cases of deformation bands were found. In general these bands had considerable internal detail, analogous to fig. 6. Our study was not sufficiently detailed to determine what proportion of the suitably oriented grains exhibited such bands.

Doubt has been expressed in some quarters that plastic flow is confined initially to the regions in which a kink develops, as would be expected if dislocation pairs were generated in the region between the band boundaries. An experiment, however, has confirmed our view of the localized nature of the slip. A crystal that had been polished before compression developed slip lines during compression at the kinked regions, but other regions were left unaltered and therefore free from appreciable plastic flow.

## The Vapor Pressures of Zinc and Cadmium over Some of Their Silver Alloys

by C. E. Birchenall and C. H. Cheng

DISCUSSION, G. P. Halliwell presiding

G. EDMUNDS—Is it possible to make even closer and more sensitive temperature determinations if, instead of going to complete evaporation of the condensate, some condensate is retained, and the increase in amount observed, thus eliminating any difficulty of forming the first droplets?

C. E. BIRCHENALL (author's reply)—I think that is certainly the case, and I thank you for the suggestion. One can get closer by spending a considerably longer time in waiting for the evaporation or condensation to occur; that is, cutting down the heating and cooling rate. On the other hand, there is probably a hysteresis to the nucleation effect, of which I hesitate to speak. Your suggestion would eliminate that effect, so that one could possibly get the equilibrium point at which the droplets neither grew nor diminished in size.

V. G. PARANJPE—What is the minimum vapor pressure that can be measured by this technique?

C. E. BIRCHENALL—I think with any convenience in operation at all, probably somewhere between a tenth and one millimeter pressure is the lower limit for this type of measurement. However, there are other methods which would not be too difficult to apply at pressures below this.

G. EDMUNDS, Metallurgical Department, American Brake Shoe Co., Mahwah, N. J.; V. G. PARANJPE, Department of Metallurgy, Massachusetts Institute of Technology, Cambridge, Mass.



# The Diffusion and Solubility of Carbon in Alpha Iron

by J. K. Stanley

DISCUSSION, R. Smoluchowski presiding

L. S. DARKEN—I should like to congratulate Dr. Stanley for this excellent contribution to our knowledge on the diffusivity and solubility of carbon in alpha iron. There has been an empty niche in the literature for quite a long time, which seems quite nicely filled by the data which has just been presented. I was particularly pleased to see that in the filling of this niche use is made of a method which involves extensive chemical analysis. Unfortunately, it seems to be the style to avoid chemical analysis; it is indeed gratifying to find that the valuable information of this paper is based on the firm foundation of a precision analytical method.

A question, perhaps beyond the scope of this paper, seems naturally to arise. One of the most obvious places to apply this data on the diffusivity of carbon in ferrite is to the decarburization of ferrite by gases such as wet hydrogen. Usually in such cases complications are introduced in the mathematics by the presence of another phase—cementite. However, the necessary modifications of the equations are available in the literature and I have made a few preliminary calculations both on the data of this paper (as represented by figs. 17 and 18) and on some of our own data and find that the observed extent of decarburization by wet hydrogen is considerably greater than that calculated from the diffusivity as determined by Dr. Stanley. It is not my intention to cast doubt on Dr. Stanley's diffusivities, which I believe are reliable. Rather, I am inclined to think that decarburization by wet hydrogen involves complications—possibly the development of fine cracks or channels. I would like to ask Dr. Stanley if he can shed any light on this apparent anomaly.

In regard to the comparison of the diffusivity of carbon in austenite and ferrite which Dr. Stanley showed on the blackboard (not in the original paper) I should like to point out that these figures by themselves may be misleading. Although in the vicinity of the eutectoid, the diffusivity of carbon in ferrite may be one hundred thirty times as great as the diffusivity of carbon in austenite, this does not mean that carbon is transported by diffusion that much faster in ferrite than in austenite. The rate of transport by diffusion is equal to the product of the diffusivity and the composition gradient (Fick's first law). For most purposes the greatest possible concentration gradient over a given distance is equal to the quotient of the solubility divided by the distance under consideration. At the eutectoid this gradient is about forty times greater for austenite than ferrite. Thus, if the same alloy could exist as either austenite or ferrite (plus cementite) at the eutectoid temperature, the rate of transport of carbon by diffusion would be only about three (130 divided by 40) times greater in ferrite than in austenite, rather than one hundred thirty times faster.

L. S. DARKEN, U. S. Steel Corp., Kearny, N. J.;  
R. F. MEHL, Metals Research Laboratory, Carnegie Institute of Technology, Pittsburgh, Pa.

J. K. STANLEY (author's reply)—This question of decarburization in wet hydrogen is very close to our hearts. There is some anomalous effect, but whether it is due to the gas reaction at the surface or in the ferrite layer, I do not know. There is a maximum in the ferrite layer width at about 825°C, and that has never been satisfactorily explained. At one time, I thought it was tied up with  $D$ , but now I am more inclined to think that the effect is due to some gas-metal reaction.

I think Dr. Darken's point about these diffusion ratios should be considered seriously, because the solu-

bilities must be considered when talking about rates of decarburization.

Let me talk, first, about the extrapolation of the  $D$  values. Van Wert, University of Chicago, determined the carbon up to about 200°C, and his  $D$  values were very close to mine; a reasonably good straight line can be drawn between his data and the values I found between 500 and 750. He thinks the activation energies may be just a bit higher, between 19,000 and 20,000, for the range from room temperature to 900°.

Of course, it is very intriguing to wonder about, what is the effect of alloy additions on the diffusion of carbon in ferrite? We are very much concerned with the effect of alloy additions and, during the past year, we have been preparing specimens of alloys containing cobalt, nickel, manganese, and a few others. However all my equipment used for the experiments just reported was moved from one room to another at the other end of the building, and it has taken about six months to set it up again. It may be that within another year or two we can get some information on carbon in alloy ferrites.

L. S. DARKEN—There is one further question I would like to raise. This concerns the rather strong effect of some alloying agents (notably molybdenum) on the rate of growth of pearlite, and the recent suggestion of Onsager that carbon may diffuse principally through ferrite rather than through austenite during pearlite formation. It has been shown that the diffusivity of carbon in austenite is not greatly influenced by the presence of small amounts of other alloying constituents; certainly the large effect of alloying elements on the rate of growth of pearlite cannot be interpreted in terms of the small effect of these elements on the diffusivity of carbon. However, if the growth of pearlite involves the diffusion of carbon through ferrite, it is conceivable that this rate of diffusion may be markedly influenced by the effect of alloying elements on the solubility of carbon in ferrite (possibly also on the diffusivity). I would like to ask whether Dr. Stanley or anyone else here sees any light shed on this old question by the new data of this paper.

R. F. MEHL—I should like to say that I think this is an extraordinarily nice piece of research. Its elegance prohibits any direct discussion but it is obvious that it offers help in many problems in ferrous metallography. I should like to comment upon one.

Several attempts have been made to calculate the rate of growth of pearlite from austenite, assuming that the rate-determining factor is the rate of diffusion of carbon in austenite. These calculations have provided rough agreement with experiments, but only at the cost of *ad hoc* assumptions and uncertain extrapolations. It was proposed by Professor Lars Onsager of Yale at the Cornell conference held in the summer of 1948 that perhaps the cementite in pearlite grows by diffusion of carbon through the ferrite (not the austenite) and that thus the rate-determining factor is the diffusion coefficient of carbon in the ferrite, known to be much greater than that in the austenite. The present data will be of assistance in this matter: good data on the diffusion coefficient of carbon in ferrite are provided; since for the amount of transport, concentration differences are also required. The work provides solubility curves which may be extrapolated.

It is clear that the concentration difference cannot be great and that, despite the high  $D$  value, the contribution to the growth of cementite from this source cannot be very great, though good calculation will be required to demonstrate the point. I might remark in passing that the Onsager proposal seems unlikely on other grounds—it would require, for example, that the  $\text{Fe}_3\text{C}$  plates would thicken as they grow, that they would be pointed at the pearlite:austenite interface, which is not observed.

This same question arises in considering the effect of alloying elements on the rate of growth of pearlite. While it has been said that alloying elements can hardly affect the rate of growth, recent extensive



measurements by Parcel, at Carnegie, have shown that both Mo and Ni do in fact decrease the rate of growth markedly, far beyond the effect to be ascribed to interlamellar spacing. Others have suggested that the retardation in the rate of growth may originate in a decrease in the  $D$  value of carbon in ferrite exercised by the alloying element, but this is highly unlikely, judging from the insensitivity of the  $D$  value for carbon in austenite to the presence of alloying elements. It would be pleasant, however, to have some direct measurements, even though no "pointing" of the  $\text{Fe}_3\text{C}$  plates is observed in alloy pearlites. Similarly, it would be good to have measurements on the effect of alloying elements on the solubility of carbon in ferrite (these would be useful in other respects, for example, in studying spheroidizing). It seems inescapable at the moment that the effect of alloying elements on the rate of growth of pearlite must originate in a necessity for the segregation of the alloying element itself, known to be very slow.

## Analysis of Interstitial Diffusion Using Activity Methods

by A. G. Guy

DISCUSSION, R. Smoluchowski

L. S. DARKEN—I should like to take issue with the fundamental nature of the author's analysis. His first equation, on which all later reasoning is based, is a pure postulate. As stated in the definition thereof,  $D_i$  is assumed to be constant. To the best of my knowledge there is, in general, no theoretical or experimental justification for such an assumption. The author makes no attempt at explicit justification.

Being unable to accept the original hypothesis, I naturally find myself unable to accept the conclusions drawn therefrom, particularly with the proposal that  $D_A$  be adopted as standard for analysis of interstitial diffusion. Fick's laws (the diffusivity  $D$  being regarded as variable) are substantially phenomenological or descriptive and devoid of assumptions. I see no point in substituting for Fick's laws, relations which involve questionable postulates. In this case I do not believe the postulate has even an approximate general validity.

In addition to the above-mentioned fundamental trouble, the suggested method involves difficulties of application which are comparable to, or even worse than, those encountered in the usual Boltzman (or Matano) solution of Fick's second law for the uni-dimensional case. Upon application of his method, Professor Guy is forced to use (or at least does use) further approximation—it is assumed that the error function is an adequate approximate solution of eq 10. Although, as shown by fig. 2, this seems approximately so for a limited concentration range of carbon in iron, I do not believe that this single case warrants generalization—in fact, on the basis of experiments in progress in our laboratory the relation does not seem valid even for higher concentrations of carbon in iron.

It is my feeling that the field of diffusion is in need, at the present time, of more and better data; in the absence of more precise data, the suggested use of unnecessary questionable hypotheses seems unfortunate.

L. S. DARKEN, U. S. Steel Corp., Kearny, N. J.; C. WELLS and W. BATZ, Metals Research Lab., Carnegie Institute of Technology, Pittsburgh, Pa.

A. G. GUY (author's reply)—Dr. Darken mentioned that, having started with the first equation, I then continued through to an inevitable conclusion. My feeling was, since the conclusion was so favorable, that the initial assumption was justified. In addition, it seems reasonable that if this corrected concentration can be used, perhaps we can avoid the variation of the diffusion constant with concentration.

Dr. Darken's second point was that the method is no

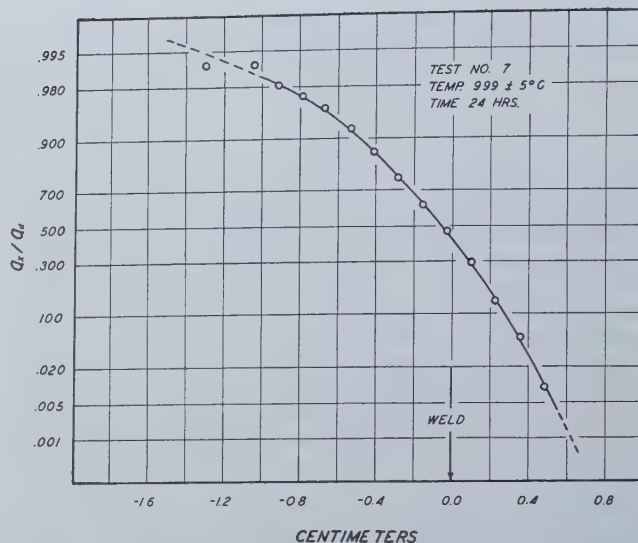


Fig. 4—Curve resulting from a plot on probability paper of  $D_i/D_s$  values against distances from the weld to centers of layers machined from the sample. Maximum and minimum limits of concentration range in the sample are 1.38 wt pct carbon (6.13 at. pct) and 0.005 wt pct carbon (0.02 at. pct), respectively.

simpler than the usual Matano type of solution. My reason for using the simplest solution in the paper, and thus introducing an additional simplifying assumption, was that the simplifying assumption produced no error that was greater than experimental error. It seemed unwise to use a more rigorous but more complicated analysis that gave the same results as a simpler analysis. The simpler analysis will be found to be applicable in many instances.

C. WELLS and W. BATZ—It appears to the present discussers that the author believes (1) the normal error-function curve drawn in fig. 2 represents rather well the distribution of carbon activity in the couple used by Wells and Mehl in their Test No. 9; (2)  $D'$  (average  $3.31 \times 10^{-7}$  cm<sup>2</sup> per sec at 1001°C) is essentially a constant over the range of carbon concentration considered; and (3)  $D'_c$  ( $2.67 \times 10^{-7}$  cm<sup>2</sup> per sec at 1001°C) is, within the limits of experimental error, also a constant independent of concentration. Providing the range of carbon concentration investigated is not too large, it does seem that these beliefs may be justified; however, recent data available to the discussers indicate that when the range of concentration is sufficiently large, the relation between carbon activity and dis-

Table IV. Values of  $D'$ ,  $Z'$  and  $D'_c$ .

Wt Pct Carbon	Carbon Activity	Distance from Interface (cm)	$D' \times 10^{-7}$ (cm <sup>2</sup> /sec)
1.22	1.50	—0.344	6.03
1.11	1.32	—0.217	5.79
0.95	1.07	—0.090	5.98
0.76	0.80	0.037	6.35
0.50	0.51	0.164	5.05
0.24	0.24	0.291	4.02
		Average	5.54

$$Z' = \frac{1.088}{1 - \frac{0.873 \times 0.23}{1.088 \times 0.975}} = 1.342$$

$$D'_c = \frac{5.54}{1.342} = 4.13 \times 10^{-7} \text{ cm}^2/\text{sec.}$$

Data are for a recent test (Test 7).

Diffusion temperature 999°C.

Diffusion time 24 hr.

In test 7, Steel 18 (1.38 wt pct carbon) was welded to Iron I (0.005 wt pct carbon)



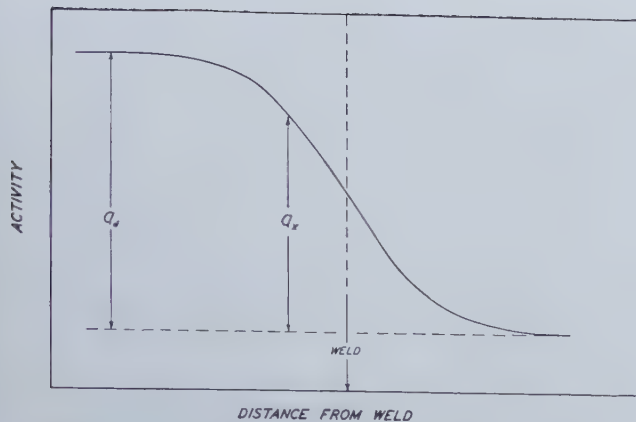


Fig. 5—Schematic activity-penetration curve showing the meaning of  $a_x$  and  $a_d$ .

tance is not correctly represented by an error-function curve and neither  $D'$  nor  $D'_c$  is a constant independent of concentration. Results given in fig. 4, table IV, and in the paper, when considered together, support these conclusions. A straight line relation between  $a_x/a_d$  (plotted on a probability scale) and distance would indicate a normal error-function relation between carbon activity and distance; a curve such as is drawn in fig. 4 shows that the relation between carbon activity and distance is not represented by a normal error-function curve and  $D'$  in this instance is not a constant. Since  $D'_c$  at 999°C, computed from data given in table IV, is not equal, within the limits of experimental error, to  $D'_c$  at 1001°C, computed from data given in the paper, it appears that  $D'_c$  varies with concentration and

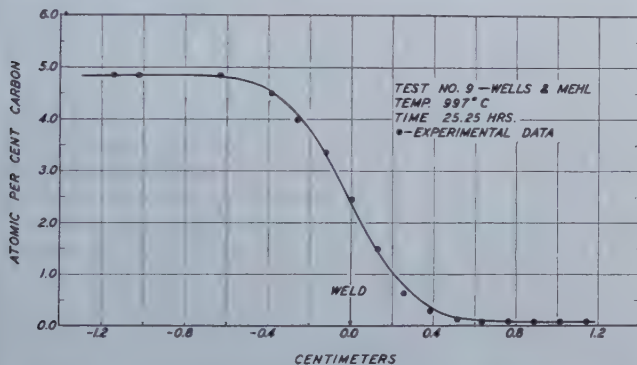


Fig. 6—Normal error-function curve based on carbon distribution data.

that this is appreciable when the concentration range is sufficiently large.\*\*

\*\* While under certain conditions the method described in the paper by the author and used by the present discussers gives values of  $D'_c$  which are approximate and higher than true values, it is thought unlikely that  $4.13 \times 10^{-7}$  cm<sup>2</sup> per sec—the estimated value when the temperature is about 1000°C and the activity 0.873 (table IV)—is higher than the true value by as much as  $1.46 \times 10^{-7}$  cm<sup>2</sup> per sec.

The meaning of values of  $a_x/a_d$  plotted in fig. 4 should be clear from fig. 5;  $a_d$  is the difference between maximum and minimum activity in the couple† and  $a_x$  is the difference between the activity at any point  $x$  on the curve and the minimum.

† Each couple consists of a steel of one carbon content welded to iron or steel of another content. During diffusion carbon flows unidirectionally from the high to the low carbon side of the couple.

In fig. 6 data are plotted from Wells and Mehl test No. 9 showing the distribution of carbon in a couple heated at 997°C for 25.25 hr; a normal error-function curve is also drawn in the same figure. It is believed the author would have less difficulty in convincing a reader that the relation between carbon activity and distance is better represented by a normal error-function curve than is the relation between carbon concentration and distance if he were to plot (1)  $a_x/a_d$  (on

a probability scale) vs. distance and (2)  $C/C_0$  (on a probability scale) vs. distance as in fig. 7, rather than (3) activity vs. distance (author's fig. 2), and (4) carbon concentration vs. distance (as in fig. 6). Of the two lines of best fit (fig. 7), A is practically a straight line while B is definitely curved.

A summary showing the relation between each of the following  $D$ ,  $D'$ ,  $D_1$ , and  $D'_c$  and concentration is given in fig. 8.  $D$  designates diffusion coefficient;  $D'$  is

from the equation  $D' = \frac{D}{\left(1 + \frac{c}{\gamma} \frac{\partial \gamma}{\partial c}\right)}$ ;  $D_1$  is from the

equation  $D_1 = \frac{D}{\left(\gamma + c \frac{\partial \gamma}{\partial c}\right)}$ , and  $D'_c$  has the meaning

given by the author. Apparently, within the limits of experimental error,  $D'_c$  varies with concentration about as much as  $D_1$ , while both  $D_1$  and  $D'_c$  vary very much less than does  $D'$ .

It is understood that Dr. Guy, who has recently re-

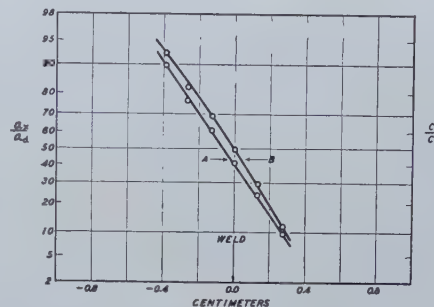


Fig. 7—Plot of  $a_x/a_d$  and  $C/C_0$  on probability scale against distance from weld.

ceived new data† covering a higher range of concen-

† Data supplied by the Metals Research Laboratory, Carnegie Institute of Technology, Pittsburgh, Pa.

tration than discussed in the paper, still believes  $D'_c$  does not vary with concentration. Perhaps the belief of Dr. Guy would be more readily accepted by many readers if he would explain the step by step method he used, especially the significance of  $K$  in the expression  $Z' = KZD'_c$ . One knows, of course, that in the equation  $\lambda_0 = X_0/\sqrt{t}$ , and for given boundary conditions  $\lambda$  is a constant when the concentration (or activity) is constant.

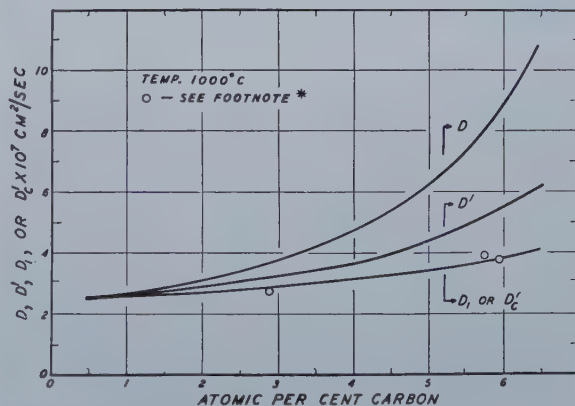


Fig. 8—Shows relation between each of following  $D$ ,  $D'$ ,  $D_1$ , and  $D'_c$  and concentration.

\* Data points, centers of circles, represent  $D'_c$  values computed from data referred to in a paper by Wells and Mehl† and from unpublished results. Data are for Tests 10, 44, and 45. In Test 10, Steel A2 (0.02 wt pct carbon) was welded to Steel B3 (1.07 wt pct carbon); in Test 44, Steel 14 (1.10 wt pct carbon) was welded to Steel 19 (1.40 wt pct carbon), and in Test 45, Steel 16 (1.27 wt pct carbon) was welded to Steel 19. It is believed that when the carbon concentration range in a couple is sufficiently small so that  $D'$  over the range may justifiably be assumed constant, then computed  $D'_c$  values at various concentrations are likely to increase with concentration about as shown in fig. 8.



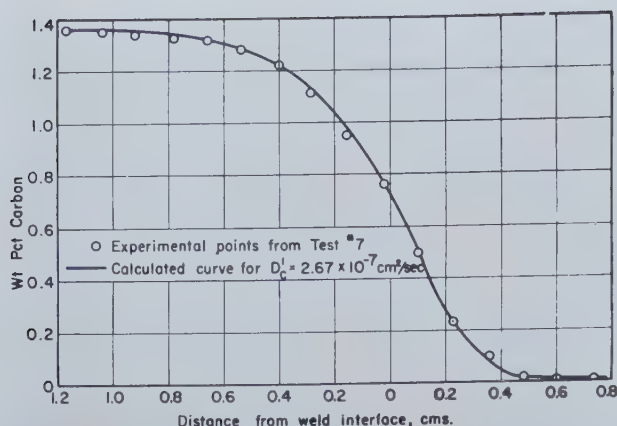


Fig. 9—Agreement between curve calculated using eq 10 and experimental points of test No. 7 of Wells, Batz, and Mehl.

A. G. GUY—Wells and Batz agree that the simple error-function solution can be used in connection with carbon activities at low carbon contents. Their discussion is a convincing confirmation of the suggestion made in the paper that this approximate solution gives poorer results at high carbon contents. However, the rigorous equation, eq 10, can be applied in these instances, and fig. 9 shows the excellent agreement between the curve calculated using this equation and the experimental points of test No. 7 of Wells, Batz, and Mehl.<sup>11</sup> Details of the calculation of this curve are given in a forthcoming paper.

<sup>11</sup> C. Wells, W. Batz, and R. F. Mehl: *Trans. AIME* (1950) 188, 553-560; *Jnl. of Metals* (March 1950) TP 2792E.

## The Study of Grain Boundaries with the Electron Microscope

by J. F. Radavich

DISCUSSION, J. B. HESS presiding

R. F. MEHL—Has the author made any morphological studies of pearlite beyond those put on the screen?

J. F. RADAVIDICH (author's reply)—In our studies we worked with a SAE 1020 and 1040 steel. We had the composition of these specimens, and we therefore used them. We have not made any morphological studies.

The oxide film replica is being used now in order to help interpret the formvar replicas. We have made some progress in understanding what occurs when a metal is heated by using the oxide film. By taking a formvar replica and an oxide film replica, we have been able to get good correlation.

I have been working with temper brittle alloy steel supplied by Carnegie-Illinois Steel Corp. The oxide film may be of great value in studies of grain boundaries and precipitation that may be located at the grain boundaries. Any type of carbide precipitation will be detected in the oxide film that forms at the grain boundaries. At the present time, we cannot say for certain that such a precipitate exists.

R. F. MEHL, *Metals Research Laboratory, Carnegie Institute of Technology, Pittsburgh, Pa.*; B. L. AVERBACH, *Department of Metallurgy, Massachusetts Institute of Technology, Cambridge, Mass.*; N. TINER, *Columbia Steel Co., Pittsburg, Calif.*

B. L. AVERBACH—Could the oxygen treatment alter the form or structure of the very fine precipitates?

J. F. RADAVIDICH—Let me say that the temperature of 650°C that I mentioned is not necessarily the only temperature for oxide film formation. We can lower

our temperature, and use an air atmosphere instead of the oxygen atmosphere. Our furnace was set at 650°C and used an oxygen atmosphere at the time of our initial studies; consequently we used it under these conditions.

We have used a 1 min replica (oxide) from 5 to 25 pct chromium alloys. We find that the carbides produce a thin oxide film which can be detected easily in the oxide film proper. We can then branch out from the carbides and interpret the rest of the replica.

N. TINER—Why is picral used to study ferrite grain boundaries with the electron microscope? Is there any relation between the grain boundary measurements and the quantity of oxygen in the steel reduced by the hydrogen anneal?

J. F. RADAVIDICH—Picral attacks the grain boundaries much more than the other usual etchants. It does not cause too much attack in the matrix which might produce structure that might cause difficulty of interpretation. Usually the etchants used are those most commonly employed in the regular metallography.

We have made no study of the relation between the grain boundary measurements and the quantity of oxygen in the steel reduced by the hydrogen anneal.

## Studies of Interface Energies in Some Aluminum and Copper Alloys

by K. K. Ikeuye and C. S. Smith

DISCUSSION, J. B. Hess presiding

J. P. NIELSEN—In this interesting paper, as well as in several other papers that are a consequence of Dr. Smith's significant and provocative paper,<sup>1</sup> there is an interchangeable usage of interfacial energy and interfacial tension for the driving forces that account for the equilibrium of interfacial configurations in metallurgical structures. This interchangeability appears acceptable as far as liquid films are concerned but does not appear to be so for solids. Solids, being fundamentally different from liquids in their arrangement of atoms at the various types of interfaces that are possible, should certainly exhibit some characteristics in the geometry of interfaces not adequately explained by the tension postulate.

In the case of annealing twins found in some microstructures, there occurs a special interface configuration which is not explainable by the tension equations introduced by Smith,<sup>1</sup> but is explainable by the interfacial energy postulate.\*

\* In an informal discussion after the meeting, C. S. Smith and J. C. Fisher suspected that the tension postulate also applies to the special twin configuration referred to in this discussion. Dr. Fisher arrived at the three equations given in this discussion on the tension postulate, i.e. similar equations are obtained by merely substituting tensions for the corresponding energies in the energy equations. Thus, the greater-than-180°-dihedral-angle case is just as readily explained by the tension postulate as by the energy postulate. The following discussion, therefore, does not give the proof that the tension postulate is not tenable for solids. Its publication is however allowed because of the proof for the stability of the special twin configuration it contains.

In fig. 21a is represented the traces of three interfaces normal to the plane of the drawing at the junction of three grains, 1, 2, and 3. On the energy postulate the equilibrium geometry is defined by the following three equations:

$$\begin{aligned} e_{12} + e_{31} \cos A + e_{23} \cos B &= 0 \\ e_{23} + e_{12} \cos B + e_{31} \cos C &= 0 \\ e_{31} + e_{23} \cos C + e_{12} \cos A &= 0 \end{aligned}$$

where the different  $e$ 's are the interfacial free energy densities for the interfaces indicated by the subscripts and which are considered essentially constant, and  $A$ ,  $B$  and  $C$ , the dihedral angles, after Smith. The three angles are the variables which are defined by these equations if the relative values of the  $e$ 's are known. Since  $A+B+C = 360^\circ$ , one of the equations is not necessary, and thus two equations suffice to define the



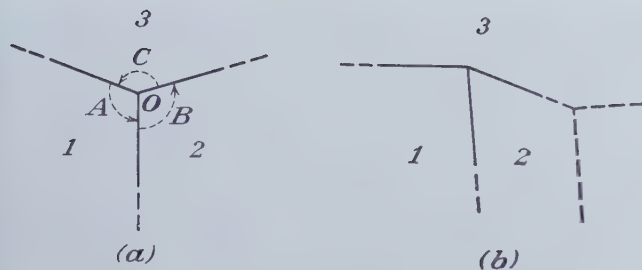


Fig. 21—Diagram of traces of interfaces.

equilibrium geometry. If we now postulate, in addition, that two boundaries are free to migrate while one cannot, for example consider trace 1-2 as the non-migrating one in fig. 21a, then the point 0 is free to move only along 1-2, either in the direction of extension, or contraction of this interface. This postulate then reduces the two equations defining equilibrium to one equation. (It is tacitly assumed that all the boundaries maintain minimum surfaces throughout the adjustment toward equilibrium, so that the traces of fig. 21 are always straight. If the traces would take on curvature in reaching equilibrium dihedral angles, then two angles remain independent for this case and two equations are still required.) On examining the first of the three equations above, it is seen that solutions can be obtained by having either the two cosines negative, or only one of them negative. The former solution requires the two angles  $A$  and  $B$ , to be both greater than  $90^\circ$ , while the latter solution requires only one greater than  $90^\circ$ . The latter solution permits angles greater than  $180^\circ$  for  $C$  when  $e_{12}$  is significantly smaller than either of the other two  $e$ 's. Thus, the configuration shown in fig. 21b can be stable for certain combinations of the interfacial energy values, which configuration is found occasionally in microstructures containing annealing twins. Smith<sup>1</sup> has pointed out that the large angle cusps found at twins indicate that twin boundary energies must be relatively small, which condition particularly satisfies the requirements of the greater-than- $180^\circ$ -dihedral-angle solution.

J. P. NIELSEN, *Department of Metallurgy, New York University, New York, N. Y.*; J. T. WABER, *Los Alamos Scientific Laboratory, Los Alamos, New Mexico*; R. SMOLUCHOWSKI, *Metals Research Laboratory, Carnegie Institute of Technology, Pittsburgh, Pa.*

J. T. WABER—Is hot shortness the same type of phenomenon as corrosion by liquid metals?

R. SMOLUCHOWSKI—The difference in the angle at both ends of the foreign phase inclusion may be due simply to the fact that the grain boundary is not flat. The two boundaries of, for instance, a "lens" shaped inclusion and the grain boundary form a closed curve. If the curve is not a circle, which will happen when the grain boundary is not flat, then the cross-section of the inclusion with the surface of the sample will, in general, produce unequal dihedral angles.

C. S. SMITH—Dr. Nielsen replies to his main argument in his own footnote. Although it is preferable to use the term "interface free energy" for the driving force behind the phenomena under discussion, it is equally permissible to use the term "surface tension." The two are mathematically identical, despite the fact that in crystalline solids there may exist surface compressional forces. For all but the most mathematically minded the tension concept is more easily visualized. Dr. Nielsen's solution of the twin boundary problem is a result of the track model that he used, which I fully accept, and is not a result of using energy in place of tension.

I completely agree with Dr. Waber that interface energy is an important factor in stress corrosion cracking, particularly by molten metals, but probably in other cases also.

## P-type and N-type Silicon and the Formation of the Photovoltaic Barrier in Silicon Ingots

by J. H. Scaff, H. C. Theuerer, and E. E. Schumacher

DISCUSSION, W. C. Ellis presiding

W. C. ELLIS—As Mr. Scaff indicated, the added constituents were present to an extent of less than one-hundredth of a percent, and yet there was a marked segregation of the phosphorus and boron, not the same for the two elements. What is known about the constitution diagram of silicon-phosphorus and silicon-boron? Are these elements in solid solution?

J. H. SCAFF (authors' reply)—X-ray studies by E. S. Greiner have shown that boron and phosphorus enter into substitutional solution in silicon. His results were reported in a recent paper by Pearson and Bardeen.<sup>10</sup>

<sup>10</sup> G. L. Pearson and J. Bardeen: *Phys. Rev.* (1949) 75, 865-883.

W. D. ROBERTSON—I should like to ask whether the temperature dependence of resistivity has been investigated and, if so, with what result.

J. H. SCAFF—Pearson and Bardeen<sup>10</sup> determined the resistivity of silicon-boron and silicon-phosphorus alloys from  $87^\circ$  to  $900^\circ\text{K}$  and interpreted the results in terms of the band theory. At elevated temperatures intrinsic conductivity is observed. In this region large negative temperature coefficients of resistance are found and the conductivity is independent of impurity concentration. At room temperature the conductivity depends upon the concentration of impurities.

W. C. ELLIS, *Bell Telephone Laboratories, New York, N. Y.*; W. D. ROBERTSON, *Institute for the Study of Metals, University of Chicago, Chicago, Ill.*; H. E. STAUSS and M. C. BLOOM, *Naval Research Laboratory, Washington, D. C.*

H. E. STAUSS—In the compensation of boron by phosphorus, do you picture that both the boron and phosphorus remain in solution and are not removed by the separation of a second phase such as an inter-metallic compound?

J. H. SCAFF—We have no evidence that the compensation mechanism involves compound formation and the separation of a second phase. We prefer simply to consider that the boron and phosphorus remain in solution and that the valence bond deficiency introduced by the trivalent atom is eliminated by the excess electron introduced by the pentavalent atom.

M. C. BLOOM—Do you get analogous phenomenon with germanium? What is the frequency response of this photo effect?

J. H. SCAFF—Analogous effects are observed in germanium. The peak in the spectral response of the  $p/n$  boundary in silicon is about 1.1 microns while that for comparable germanium boundaries is about 1.6 microns.

## Microstructures of Silicon Ingots

by W. G. Pfann and J. H. Scaff

DISCUSSION, W. C. Ellis presiding

C. S. SMITH—As the authors point out, the location and general shape of the banded-structure zone show that it must bear some relation to the interface between solid and liquid, advancing during solidification. It seems to be quite independent of crystallographic features. Is it possible that the structure is related to Liesegang rings, and is a result of successive supersaturation, nucleation, precipitation, and depletion of some constituent of very low diffusion rate?

W. G. PFANN (authors' reply)—While we cannot be definite about the exact nature of the striae, the best evidence we have indicates that they are the result of variations in solute concentration in the solid produced during the freezing process. It will be noted that although faint striae are visible throughout the  $p$ -type



and *n*-type regions, the markings are much sharper at the *p*-*n* barrier. The accentuated etch-attack at the barrier may possibly be an electrochemical etching effect arising from the photovoltaic properties of the barrier.

J. F. RADA VICH—In working with the electron microscope at Purdue, we have found some interesting things about germanium, in particular, at these *p*- and *n*-type areas. We have found that in the cathodic etching of the material, where the metal is sputtered off, there is a very different type of grain boundary than when the etchant is an acid. I suggest that you might try this cathodic etching.

We observed not one grain boundary but a grain boundary area made up of three different types of structure. The crystallographic structure of the first part of the grain boundary was oriented at an angle of 45°, and this layer was followed by a band of structureless material. The third part of the grain boundary was similar to the first band in crystallographic structure, but it was oriented at an angle of 90° to the first band.

C. S. SMITH, *Institute for Study of Metals, University of Chicago, Chicago, Ill.*; J. F. RADA VICH, *Department of Physics, Purdue University, Lafayette, Ind.*

W. G. PFANN—Dr. Radavich's statement brings to mind other features of these microstructures. We have found rather unusual etch patterns in certain parts of the ingots, particularly in the *n*-type regions, for example, quite perfect hexagons, and a structure resembling shingles on a roof. It is interesting that shingle-like etch patterns were reported in 1905 by Albro in the Transactions of the American Electrochemical Society. Another means of showing up the *p*-*n* barrier has been used by H. C. Theuerer. The method is to immerse a *p*-*n* barrier specimen in a copper-plating solution, making contact, with forceps, only to one side of the barrier. The copper plates out only on the side held in the forceps. Because of the electrical resistance of the *p*-*n* barrier, the other side does not become plated.

## Electrical Properties of the Intermetallic Compounds $Mg_2Sn$ and $Mg_2Pb$

by W. D. Robertson and H. H. Uhlig

DISCUSSION, A. Jones presiding

J. H. SCAFF—Are any rectification or photoelectric effects observed when these materials are applied to other metals?

W. D. ROBERTSON (authors' reply)—Possible photoelectric effects were not investigated. Rectification efficiency is low, though the method used was inadequate and this property should be redetermined.

M. A. STEINBERG—I talked to Dr. Robertson concerning the difficulty of melting and casting these intermetallics to obtain compounds of the correct stoichiometric composition. We have tried several procedures and one method that seems to work, if one is only interested in very thin layers of the intermetallic, is diffusion treatment.

In the case of magnesium and tin, two ½-in. diam disks were used, one being placed on the other in a ½-in. diam hole in a graphite boat. A weight was placed on the disks and they were heated over the melting point of the tin but under the melting point of the magnesium. After the diffusive treatment, the disks could be easily split apart at the interface and a very thin layer of intermetallic was found to be present on the contact surface of the magnesium. This procedure has been used successfully to form thin

J. H. SCAFF and W. C. ELLIS, *Bell Telephone Laboratories, New York, N. Y.*; M. A. STEINBERG, *Horizons, Inc., Cleveland, Ohio.*

layers of the intermetallics of magnesium with Sn, Pb, Bi, and Sb, and a thin layer has been found in most cases to be present on the contact surface of the more refractory metal.

W. D. ROBERTSON—The difficulty in diffusion methods of preparation is precipitation of the compound at the interface which, because there is essentially no solid solubility, acts as an impervious barrier to further diffusion and formation of the compound. In fact, this method was used by Hume-Rothery<sup>10</sup> to

<sup>10</sup> W. Hume-Rothery: *Jnl. Inst. Metals* (1927) 38 (2), 127.

prove the absence of solid solubility in the  $Mg_2Sn$  compound; he immersed magnesium in molten tin for some weeks and obtained only a microscopically thin surface film which did not penetrate further on re-immersion for a considerable time.

We attempted to prepare  $Mg_2Si$  by analogous methods but without success. However, we did not apply pressure which, in Dr. Steinberg's method, apparently breaks the film allowing further reaction to take place. This method does not produce the compound in a form permitting an absolute measurement of conductivity which is necessary for an adequate evaluation of electrical properties. It may, of course, be sufficient for a determination of rectification but, in that case, there may be some question regarding the composition at the point of contact.

W. C. ELLIS—It is suggested that metallic type conduction in  $Mg_2Pb$  is due to the lead atom being incompletely ionized; it therefore exhibits a valence of less than four.

W. D. ROBERTSON—The question of the metallic conductivity of  $Mg_2Pb$  is one of the significant aspects of this work. It seems that there are two possibilities. Either the energy gap is so small that a limited number of electrons are promoted at room temperature, or the assumption of quadrivalent lead is inaccurate. According to Pauling's theory the latter is probably correct but it is then somewhat difficult to explain the high resistivity which indicates that electrons are not as free to move as in a typical metal. No conclusive answer can be given until more data are available.

## Ferromagnetic Alloys in the Systems Cu-Mn-In and Cu-Mn-Ga

by F. A. Hames and D. S. Eppelsheimer

DISCUSSION, A. Jones presiding

R. I. JAFFEE—In some work I did sometime ago on nickel manganese alloys, on the ordered alloy,  $Ni_3Mn$ , I noticed that the quality of magnetism developed, hard or soft ferromagnetism, was markedly effected by manganese content. On the low manganese side, the ferromagnetism was soft, and on the high manganese, the ferromagnetism was quite hard. I wonder if that might also occur in the present type of ordered ferromagnetic alloys containing manganese?

F. A. HAMES (authors' reply)—I do not know.

R. I. JAFFEE, *Battelle Memorial Institute, Columbus, Ohio.*

## The Beryllium-iron System

by R. J. Teitel and M. Cohen

DISCUSSION, P. A. Beck presiding

H. MORROGH—The point of particular interest in this paper concerns the structures obtained containing the eutectic which, according to these investigators, occurs at 77 pct beryllium and 1225°C.

Fig. 13 shows the structure of a sample containing 1 at. pct iron with large primary grains of theta with epsilon representing the degenerate eutectic. In fig. 14,



taken from an alloy containing 2.3 at. pct iron, the degeneration of the eutectic is less pronounced and it can be seen that in the eutectic the epsilon is the continuous phase. I find that it is usually possible to say, in most binary eutectics, that one phase is the dispersed phase and that the other is the continuous phase. Furthermore, it seems that when the primary deposition corresponds to the dispersed phase of the eutectic, degeneration of the eutectic can occur. This is in line with the structure shown in the two micrographs referred to above. However, in fig. 16, showing the structure of an alloy containing 5.2 at. pct of iron (this alloy being, as it were, from the other side of the eutectic) we have primary epsilon together with the eutectic. In this case, however, if the description is correct, the epsilon appears to be the dispersed phase and the theta appears to be the continuous phase.

H. MORROGH, *The British Cast Iron Research Association, Birmingham, England.*

I am wondering whether there could have been some mistake in the reproduction of these micrographs or whether the structures and the equilibrium diagram are exactly as described by the authors, since in my experience it appears that one can state as a general rule that the dispersed phase remains as such regardless of the type of primary phase which is present. Based on this general theory, one would have expected that the structure shown in fig. 16 represented primary theta surrounded by the eutectic, and therefore if the alloy contains 5.2 at. pct of iron, then the eutectic point under consideration must be in a different position from that indicated by the authors.

On the other hand, if the facts presented by the authors are absolutely correct, then we have an interesting case (perhaps even an anomalous case) of a eutectic, the dispersed phase of which varies according to the nature of the primary phase present.

R. J. TEITEL and M. COHEN (authors' reply)—We agree with Dr. Morrogh that the matrix and dispersed phases of a binary eutectic usually remain as such, irrespective of the primary phase coexisting with the eutectic. This means that there is no fundamental change in the state of aggregation of the eutectic structure whether the alloy composition is on one side or the other of the eutectic composition.

However, this rule may break down in the case of "degenerate" or "divorced" eutectics. Such instances tend to occur at compositions near the primary phases, where the corresponding phase of the eutectic crystallizes on the large quantity of primary phase present and leaves an excessive amount of the second phase in the remaining (degenerate) eutectic. In our experience, such degeneracy is by no means confined to the side of the diagram on which the primary phase corresponds to the dispersed phase of the eutectic.

While it may be true that degeneracy occurs *more readily* when the primary phase is the same as the dispersed phase of the eutectic, nevertheless this phenomenon may also occur when the primary phase is the same as the matrix phase. In fact, the latter situation may so reduce the amount of the normal matrix phase in the eutectic, and may so alter the solidification of the remaining eutectic, that the normally dispersed phase becomes the matrix of the eutectic.

It should also be emphasized that our beryllium-rich alloys solidify as ternary rather than binary compositions (fig. 10). This may complicate the matter still further, and render it quite risky to place too much weight on the state of aggregation of the eutectics as observed. Dr. Morrogh has described the micrographs correctly; there is a change in the matrix phase of the eutectic from theta (normal) to epsilon when the iron content is so low that an excessive quantity of the eutectic theta crystallizes on the predominating primary theta. This causes the epsilon to become the matrix of the degenerate eutectic in figs. 13 and 14, in contrast to the normal theta matrix in the higher iron alloys of figs. 15 and 16.

In view of the foregoing, we believe that the microstructures are consistent with the diagram as published. Moreover, we have been unable to conceive of any other diagram which would account for the many thermal and X-ray determinations.

## Solubility of Titanium in Liquid Magnesium

by K. T. Aust and L. M. Pidgeon

DISCUSSION, T. E. Leontis presiding

W. C. LILLIENDAHL—Is there any information on the solubility of magnesium in titanium?

K. T. AUST (authors' reply)—There was no experimental work done on the high titanium end of the system. Results were obtained only for the low titanium side.

G. EDMUNDS—In table I the last two columns headed "Pct," and "Titanium," respectively, should be under a single heading "Pct Titanium" according to the authors since these columns are duplicate analyses of the same specimen. In the middle of the table under "Holding Time, Hours," no holding time is given for the first four figures because, according to the authors, these are not liquid samples but were taken from the tops of the other billets after they had solidified and that is where the temperature figures 651 arise. Regarding this paper and the one by Nelson and Sager, has the method introduced by Fink and Freche<sup>15</sup> of testing the results of liquidus determinations been used?

W. C. LILLIENDAHL, *Westinghouse Research Co., Bloomfield, N. J.*; G. EDMUNDS, *American Brake Shoe Co., Mahwah, N. J.*

K. T. AUST—The method introduced by Fink and Freche was applied to the liquidus results obtained for titanium in magnesium at 700°C, 775°C, 850°C. Using these limited number of values, a straight line plot was obtained between the log of the at. pct of Ti in Mg vs. 1/T.

A letter to the author from A. C. Loonam, New York, N. Y., indicates that earlier data on this subject was available in the literature.<sup>16</sup> Notes taken on this reference indicated that molten magnesium was treated with sufficient titanium tetrachloride to yield an alloy containing 10 pct titanium. After all of the TiCl<sub>4</sub> had been added, the supernatant metal was cast. It was found to contain 0.08 pct Ti. Much of the residue remained solid in the crucible and did not melt, even at temperatures so high that the magnesium volatilized and caught fire. This work was probably only of a qualitative nature but it does confirm the Aust and Pidgeon conclusions regarding the relatively low solubility of titanium in molten magnesium.

### References

- <sup>15</sup> W. L. Fink and H. R. Freche: *Trans. AIME* (1934) 111, 304.
- <sup>16</sup> Grogan and Schofield: Influence of Volatile Chlorides on Magnesium and Copper. *Jnl. Inst. Met.* (1933) 51, 123.

## Liquid Solubility of Manganese in a Magnesium-aluminum-tin Alloy

by B. J. Nelson and G. F. Sager

DISCUSSION, T. E. Leontis presiding

G. ANSEL—Have the authors compared the solubility curve of manganese in molten AM65 alloy with the solubility curve of manganese in a molten Mg-3.5 pct Al alloy?

G. ANSEL, *Magnesium Laboratories, Dow Chemical Co., Midland, Mich.*; G. EDMUNDS, *American Brake Shoe Co., Mahwah, N. J.*



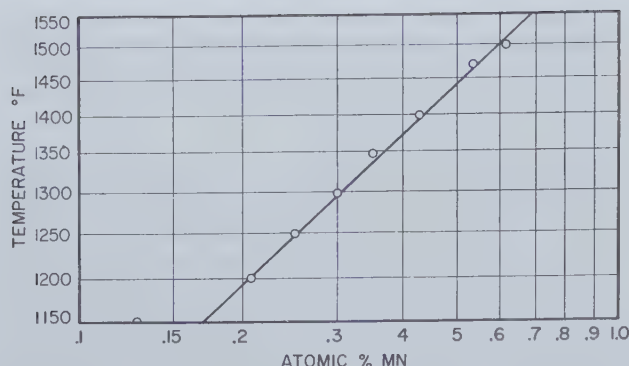


Fig. 5—Solubility of Mn in molten AM65S.

B. J. NELSON (authors' reply)—We have made such a comparison. At any given temperature, the liquid solubility of manganese in AM65S is lower than that in alloys of comparable aluminum content, indicating that tin depresses the solubility of manganese.

G. EDMUNDS—Have the authors plotted their results as the log of the atomic percent against the reciprocal of the absolute temperature?

B. J. NELSON—Yes, such a plot is shown in fig. 5.

## A Metallographic Description of Fracture in Impact Specimens of a Structural Steel

by M. Baeyeritz, W. F. Craig, Jr., and E. S. Bumps

DISCUSSION, J. J. Heger presiding

J. A. KIES and G. R. IRWIN—We are gratified to see this paper as an example of better descriptions of fracture which are rapidly appearing in the literature. It is especially important to have pointed out the

The opinions expressed herein are those of the writers and do not necessarily reflect the views of the Navy.

similarities which are to be found on fractures in mild steel broken at different temperatures. It is these similarities which lead us to believe that a good understanding of fracture mechanisms is not too difficult to achieve. The authors have performed a valuable service in explaining fractographic features in terms of dynamic effects, for example, the rumpling of cleavage facets by plastic flow. We hope that someone will relate this action in a quantitative way to the delay time for plastic flow already studied by Clark and Wood.<sup>6</sup>

The authors could have referred to much additional work to support and amplify their view of the discontinuous nature of fracture, notably that of Ellinger and Williams,<sup>7</sup> of Tipper,<sup>8</sup> and of Shevandin.<sup>9</sup>

The authors' interpretation of fig. 3a and b should probably not be taken as proof that complete absence of plastic action existed on the cleavage facets of specimens labeled 100 pct brittle.

On figs. 3a, b, c, and d may be found dark lines which represent level differences between adjoining smoother portions of the fracture. It can be shown that these different levels are produced by separately initiated or nucleated fractures. The main reason why this may not be obvious is the remarkably fine scale on which the nucleations usually occur in such brittle fractures. Although the lines in figs. 3a and b are relatively straight they differ little in origin from those in 3c and d. We like to call this feature the river system. The fracture travels with a scalloped front in the general direction of combining tributaries. These are prom-

inent in fractures of glass and hardened steel as well as on cleavage facets of crystals.

The origin of the separate tributaries may be conveniently studied by using samples of plastics purposely molded or otherwise conditioned to produce gradually varying degrees of brittleness. Our fig. 19, taken at X1000, shows an example of fracture nucleation in lucite. The sharp lines mark off different parts of the fracture at different levels. Ample evidence exists to prove that the parabola-like figure was generated by the interference between a fracture nucleated at its focus and the main fracture coming toward it. The lines or streamers under suitable conditions combine as tributaries to form the familiar river system.

An example of the effect of a flaw is shown in fig. 20. Miss A. M. Sullivan of the Fracture Studies Group prepared this to show almost identical structures in tool steel and in cellulose acetate. Both views show a nucleated fracture having originated from what appears to be a hole. This need not be surprising, but the observation that this feature can be found again and again on finer and finer scales, as far as optical resolution will permit, leads us to believe that fractures, however brittle, contain uncountable numbers of localities in which it is reasonable to assume that plastic action may have occurred around nucleating flaws. The conclusions of Gough regarding his experiments on antimony single crystals<sup>10</sup> could similarly be reinterpreted. He stated that although no slip was observed, fracture did initiate on planes that one would normally expect to be slip planes. We maintain that complete absence of slip, at least locally, is not established by anyone's failure to observe it in a particular

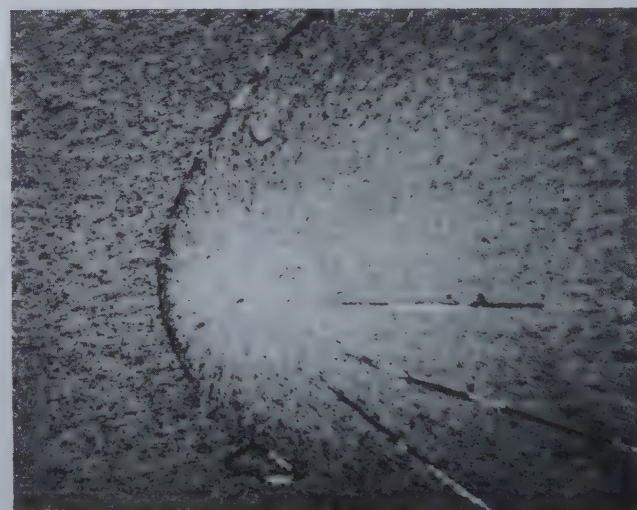


Fig. 19—Large parabola with small-scale components in lucite.

X1000. Area reduced approximately three fourths in reproduction.

attempt by ordinary microscopy—even in crystals not supposed to have slip planes in the usual sense.

The mechanism of joining separately nucleated fracture components will be discussed in a forthcoming paper by members of the fracture studies group at the Naval Research Laboratory.

L. D. JAFFE—I would like first to compliment the authors on this very excellent piece of metallographic work. They found the transition temperatures of the transverse and longitudinal specimens to be essentially the same. They were studying a structural steel. Our experience has been primarily on heat-treated alloy steels, and on these materials we have generally found that the transition temperature is significantly higher for the transverse specimens than the longitudinal. Would the authors care to comment on this?

R. H. ABORN—To commend a technical paper has become a rather trite custom, nevertheless in this instance it is most certainly warranted, for this paper

J. A. KIES and G. R. IRWIN, Naval Research Laboratory, Washington, D. C.; L. D. JAFFE, Watertown Arsenal, Watertown, Mass.; R. H. ABORN, Research Laboratory, U. S. Steel Corp., Kearny, N. J.; G. A. MOORE, Department of Metallurgy, University of Pennsylvania, Philadelphia, Pa.; W. H. BRUCKNER, Department of Metallurgical Engineering, University of Illinois, Urbana, Ill.



**Fig. 20—The effect of a flaw within crystal in tool steel produces a fracture pattern almost identical with one found in a brittle fracture in cellulose acetate.**

X500. Area reduced approximately five ninths in reproduction.

a. Cellulose acetate      b. Tool steel



gives us the first lucid and convincingly documented introduction to the nature of fracture in notched bar tests.

There is only one point on which I believe a word of caution is in order. This has to do with an implication in the summary that pearlite may be a crack arrester, acting as a barrier to the propagation of fracture in ferrite. I suggest that this is probable only when pearlite is a minor constituent as in mild steel. When it becomes a major constituent as in medium and high-carbon steels, it absorbs less energy than ferrite in fracturing, and its transition temperature in eutectoid steel is much above that of mild steel.

It is to be hoped that the authors will continue the excellent work they have begun.

G. A. MOORE—This paper represents an important and logical forward step toward the development of a metallography of fractured surfaces, a field which should attract far more attention than it has yet received. I am pleased that the authors have chosen to promote the development of this subject.

As this type of study is so little known, it would appear desirable to point out a few places where possible misinterpretations might occur. The discussion of fig. 3 might appear to imply that there is a progressive and characteristic change of the cleavage appearance with the degree of brittleness of the specimen. I do not believe this is intended, as in the work mentioned in ref. 4 it was clear that most of these appearances could be found on occasion in a single specimen. The abundance of the regular and irregular cleavages presumably changes through the series of specimens, but since it is not convenient to examine more than a few facets of the specimen in detail, it may be important to note that these few may sometimes be misleading.

The interpretation of lines, such as the presumed slip lines of fig. 3f, and *g* (*h*?) requires great care. It is possible to limit the crystallographic families to which such lines can belong by measurement of angles in the photographs. Such measurements of lines in the micrographs published in ref. 4 have shown that assignment to known slip systems cannot be justified, except in limited cases. There is considerable evidence that many of the nonrectangular markings should be assigned to imperfections existing within the grain before the start of deformation. The general fact of distortion or plastic flow in the less brittle specimens is not, however, open to serious question.

In the light of considerable other evidence which has already appeared on cleavage failures in mild steel, this paper would appear to be conclusive demonstration that the failures are in fact in the ferrite bands. While the reduction of banding thus would appear desirable toward solving the practical difficulty, it does

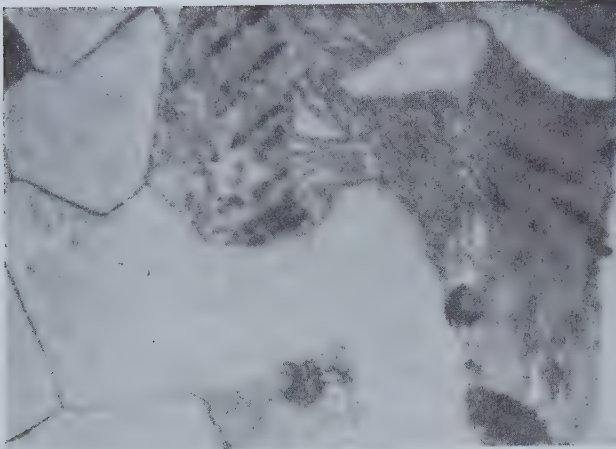
not yet appear to be time to conclude that such brittle cleavage is *inherent* in ferrite. It might be noted that no hydrogen analysis is given in this paper, and that the implied size of the piece studied indicates that the hydrogen should not be below the danger limit. Other impurities also may be suspected of embrittling the ferrite, and, of the elements reported, neither the phosphorus nor the silicon, while low, can as yet be eliminated from suspicion. The search for the reasons behind the brittleness of the ferrite should therefore be continued. It appears that the methods demonstrated in this paper may be very helpful in this search, and it is to be hoped that its authors will extend the work to include this phase of the problem.

W. H. BRUCKNER—This is an interesting study and as the authors had hoped it adds “a little to the growing fund of experimental observations of the nature of fractures in steel.” The recording of the macro and microstructures in the photographs shown in the paper gives evidence of the careful procedures and beautiful techniques of the authors. The use of a heavy nickel plate is also shown to give ideal edge protection, although somewhat better contrast with the ferrite would have been desirable.

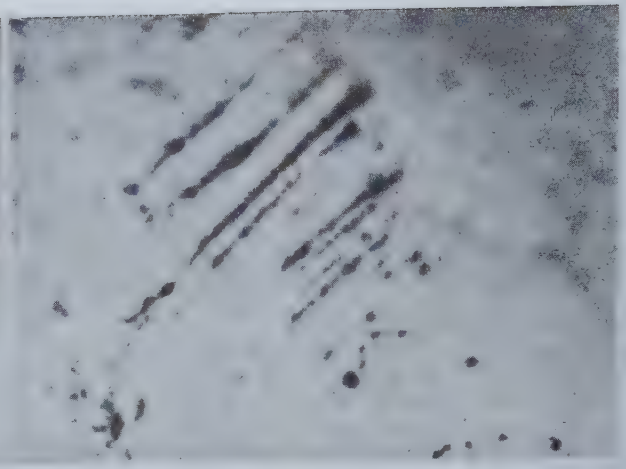
However, the information one gets from such a study depends upon the interpretation of the observed microstructure and I should like to suggest that other interpretations of some of the authors' micrographs may be different from their own interpretation and just as reasonable. This whole problem of fracture as observed under the microscope is difficult to resolve because of the disposition of a crack system in three directions while the plane of polish for metallographic examination resolves only two of these directions. The start of the crack system may be hidden in the metal lying under the polishing plane or in the metal removed during polishing. Therefore, it would appear most useful to develop a method of first identifying the crack system in three dimensions, then using the metallographic method to identify its microstructural path. No doubt the authors share with others the wish that such a method were available. The fact that a crack system ends at a certain microconstituent cannot be interpreted as evidence that the crack was stopped by the microconstituent. The crack may have been started by the particle or in an area surrounding it. It would seem therefore just as reasonable to interpret portions of the authors' micrographs of figs. 8, 9, 11, 17, as indicating that the cleavage fracture is initiated somewhere within the pearlite grains from which the cleavage spreads in ferrite grains bordering the pearlite.

I should like to cite some observations from my own work in the same field as that of the authors. The metallographic work which I have conducted is a by-





**Fig. 21—Sample tested at 77°F with 27.1 ft-lb initial energy.**  
5 pct Nital Etch. X2000.



**Fig. 22—Sample tested at 77°F with 25.6 ft-lb initial energy.**  
Unetched. X2000.

product of a program of axial tension impact tests of structural steels which has in part been published.<sup>11</sup> A cylindrically notched specimen was used to confine fracture to a definite region under the notch. Since the specimen is stressed in tension there is not the probability always associated with the Charpy impact specimen of compressional deformation having preceded deformation in tension at least in one half of the specimen volume under the notch. In the axially loaded specimen the principal stress direction is known, as is its orientation with respect to the fracture microstructure observed. Furthermore, such a specimen may be loaded in impact at any desired energy level above or below the energy required for fracture. Under these conditions, I have been able to obtain specimens which under the microscope illustrate the actual sequence of fracture. This study is almost completed and will be published in detail in the near future. A few observations on the study are given as follows:

Fig. 21 shows the typical first stage of fracture in the pearlite lamellae which is always observed in the region of the transition temperature in pearlite colonies for which the carbide lamellae are oriented parallel with the principal stress or at a maximum angle somewhat less than 45° to the principal stress. The principal stress is always in the top-to-bottom direction in the micrographs shown. The unetched microstructure shown in fig. 22 gives proof that an actual fracture exists. A carbide etch further revealed the locus of the incompleting fractures to be the carbide lamellae. Carbides at ferrite grain boundaries were also found to be regions of initial fracture, fig. 23. Later stages of fracture involving cleavage at, above, or below the transition temperature appear to be associated with

the initial pearlite fracture although at temperatures below the transition there is a lower frequency of such association. At lower temperatures twin-generated cleavage becomes quite frequent. An example of the latter is shown in fig. 24, in which two sets of mechanical twins are shown with a cleavage fracture originating at the intersection of the twins. The cleavage fracture is identified as such by means of the corner of the incompletely developed etch pit shown in the center of the field. The cleavage is parallel with (100) one of the sides whereas the twins are parallel with the diagonals (111) or (110) of the cube.

Incidentally, fig. 24 shows that twins do not go through lamellar pearlite while the cleavage fracture does.

The question of whether cleavage follows or precedes twinning is answered in fig. 25 in which three sets of twins appear in a ferrite grain with a cleavage crack across the twins. The twins have translated across the faulting plane of cleavage thus showing that the twinning occurred first and cleavage followed.

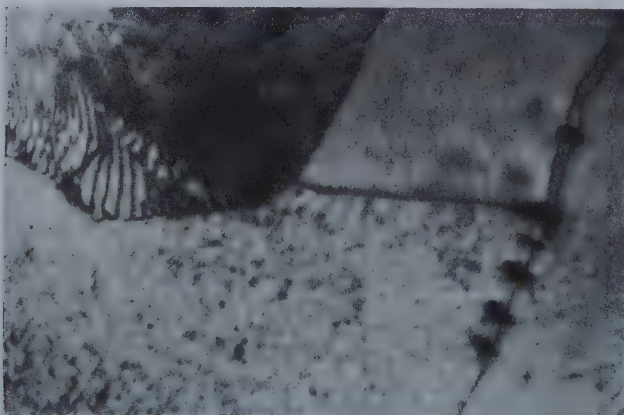
M. BAEYERTZ (authors' reply)—The authors wish to thank those who have discussed this paper. They appreciate very much the additional information on fracture that has formed a large part of some of the discussions.

We are indebted to Dr. Kies and Dr. Irwin for the references which they have supplied. We agree with them that the cleavage facets in our fig. 3a were formed by nucleation and propagation of cleavage cracks, and that the formation of the cleavage facets in this figure may involve plastic deformation on a scale that cannot be detected by ordinary metallographic techniques. We did not intend to imply that, because we had not observed it, such deformation could not be present. Our purpose was to point out the microscopically observable differences in the appearance of the cleavage facets that was brought about by raising the temperature in notched bar impact tests of a structural steel.

With regard to Dr. Jaffe's question, the essential coincidence of the longitudinal and transverse transition temperatures observed in this work applies of course to the as-rolled condition of a structural steel. We are not prepared to say that this situation maintains in heat-treated alloy steels; and in view of Dr. Jaffe's comment, it appears that it does not.

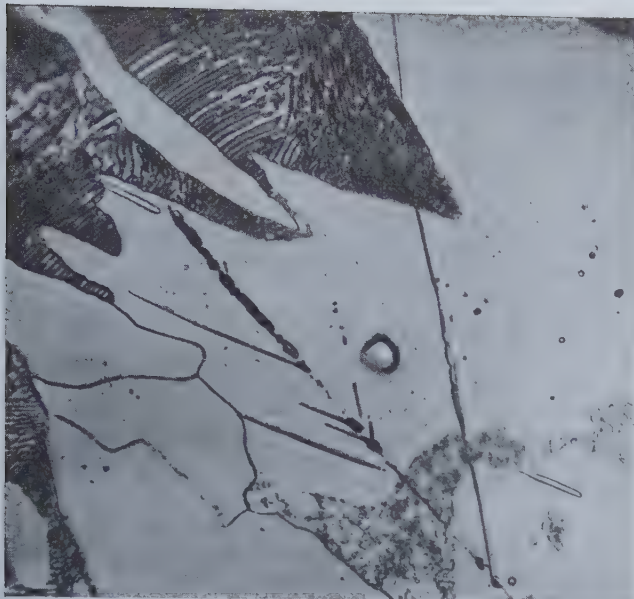
Dr. Aborn's word of caution on pearlite as a crack arrester is certainly in order. As he pointed out, our observation applies to a banded structure of ferrite and pearlite in mild steel. There, the pearlite bands appear to arrest the propagation of cleavage started within the ferrite bands. Stress distribution on loading such a banded structure is different on a microscopic scale than is the case where carbide is more uniformly distributed, as in a wholly pearlitic structure.

While not in entire agreement with some of Dr. Moore's contentions, our observations represent only a



**Fig. 23—Sample tested at 20°F with 13.8 ft-lb initial energy.**  
5 pct Nital Etch. X4000. (Area reduced approximately four ninths in reproduction.)





**Fig. 24—Sample tested at 40°F with 14.8 ft-lb initial energy.**

5 pct Nital Etch. X1000. (Area reduced approximately one half in reproduction.)

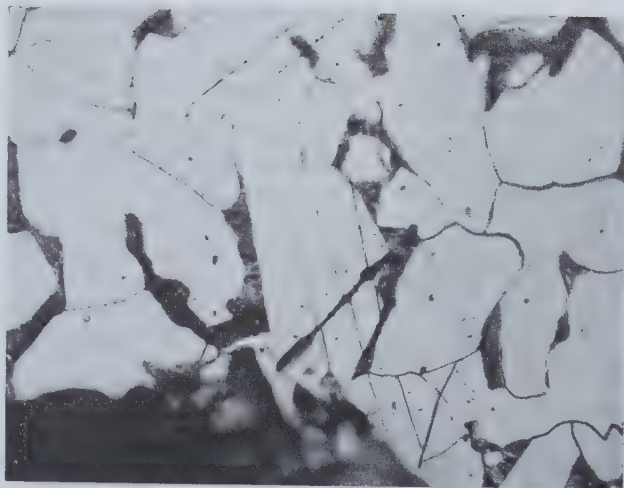
small addition to a growing but as yet incomplete knowledge of fracture, leaving plenty of room for discussion. However, we do wish to state that we observed a progressive and characteristic change in the microscopic appearance of the cleavage facets of the macroscopically "brittle" portion of impact specimen fractures as the testing temperature was raised through the transition range. Moreover, this observation was based on examination of a large percentage of the cleavage facets on each specimen. In each fracture, there was some range in the appearance of the cleavages, as illustrated by our figs. 3d and e, and 3g and h; but careful observation failed to establish a wider range of appearance than that illustrated by these figures.

The question whether brittle cleavage is "inherent" in ferrite is one to which metallurgists have devoted considerable attention. We used "ferrite" to designate the body-centered, iron-base solid solution crystals present in as-rolled structural steel. Silicon and phosphorus were present in this solid solution; quite possibly, hydrogen also. Defining ferrite in this way, it does appear to have a tendency to cleave. This is not to say, however, that the silicon, phosphorus, and hydrogen contents will not influence this tendency, for it is already well known that they do.

We are gratified, indeed, to have Professor Bruckner's comments and the additional information which he presented from his own investigations. We believe that the stress-strain relations in the tests cited from his work are somewhat different than in our tests, and that this may account for the apparent discrepancy in the two sets of observations. We are heartily in agreement that three dimensional observations are necessary, and hope eventually to be able to surmount some of the difficulties encountered in such observations.

#### References

- <sup>1</sup>D. S. Clark and D. S. Wood: Time Delay for the Initiation of Plastic Deformation at Rapidly Applied Constant Stress. A.S.T.M. Preprint 25 (1949).
- <sup>2</sup>G. A. Ellinger and M. L. Williams: National Bureau of Standards Repts.: On the Examination of Fractured Plate from S.S. George Crocker (Nov. 1, 1945); On the Examination of Section of Hull Plating from U.S. C.G.C. Northland (Date not given); On the Examination of Fractured Plates from S.S. Sea Bass (Dec. 28, 1945); On the Examination of a Fractured Plate from the S.S. John P. Altgeld (Aug. 10, 1945); On the Examination of Two Fractured Plates from S.S. Esso



**Fig. 25—Service fracture in slip plate.**  
5 pct Nital Etch. X500.

Willmington (Sept. 7, 1945); On a Fractured Plate from S.S. Enos A. Mills (Oct. 5, 1945); On the Examination of a Shear Strake Crack Arrestor from S.S. William Floyd (Feb. 27, 1946); On the Examination of a Fractured Plate from S.S. Simon Willard; On the Examination of a Fractured Plate from S.S. Maria Sanford.

<sup>3</sup>C. F. Elam Tipper: The Fracture of Mild Steel Plate. Rept. No. R3, Admiralty Ship Welding Committee, London (1948).

<sup>4</sup>E. Shevandin: The Spreading of a Brittle Fracture Crack. *Tech. Phys. U.S.S.R.* (1938), 5, 279-287.

<sup>5</sup>H. J. Gough: *Proc. Roy. Soc.* (1930) **127 A**, 431-453.

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## The Effect of Ferrite Grain Size on Notch Toughness

by J. M. Hodge, R. D. Manning, and H. M. Reichhold

DISCUSSION, J. J. Heger presiding

R. J. GREENE—Referring to fig. 14, it is surprising to find the impact values at  $-150^{\circ}\text{F}$  so low for a  $3\frac{1}{2}$  pct nickel steel of No. 5 grain size. Would these values be improved had a heat-treated steel of the desired grain size been tested rather than the as-rolled material?

S. J. ROSENBERG—I would like to ask the authors whether or not the results presented by them have been checked by tests on additional heats of steel of similar chemistry. The reason I ask this is because many years ago we did some work at the Bureau of Standards in which we studied the effect of heat treatment upon the notched bar impact toughness of a series of SAE 1050 steels. We had six steels altogether, three of them aluminum-killed and three silicon-killed, and found that the impact properties of the individual heats varied widely. It seemed as if each heat of steel had its own characteristic impact-temperature curve and, strange as it may seem, the deoxidation practice had no discernible effect upon the toughness of the steels as heat treated. Because of the variations in impact properties frequently found in presumably similar steels, I believe that in any work of this nature it is a good idea to include samples from a few additional heats of similar steel, if only for a spot check.

R. J. GREENE, Bayonne Laboratories, International Nickel Co., Bayonne, N. J.; S. J. ROSENBERG, National Bureau of Standards, Washington, D. C.; I. R. KRAMER, Materials Branch, Office of Naval Research, Washington, D. C.; M. A. SCHEIL, Metallurgical Research, A. O. Smith Corp., Milwaukee, Wisc.



I. R. KRAMER—Was any change in yield point noted, especially for the nickel steels where no change in impact transition temperature was found? Did the elongation at the yield point change with nickel content or with grain size?

M. A. SCHEIL—Our experience with commercial rolled plates of 3 to 3½ pct nickel steel of about 0.10 to 0.20 pct carbon indicates that sometimes a single or double normalizing is required to obtain Charpy impacts of 15 ft-lb at -150°F. With 8½ pct nickel steel at subzero temperatures generally the Charpy impact values are higher when carbon is below 0.10 pct. Have the authors tried normalizing their low-carbon steels?

J. M. HODGE (authors' reply)—In regard to the energy level at -150°F, we have also observed, of course, that these transition temperatures in the 0.02 carbon steel are considerably higher than those of commercial nickel steels. We certainly do not yet understand the reasons for these differences, but we believe that they may be, to a considerable extent, a reflection of the higher carbon content of the commercial steels.

Mr. Rosenberg has asked whether we tried the same thing on other steels. We have not exactly, but we have studied the transition temperatures of other steels as a function of variables such as austenitizing temperature and to a certain extent cooling rate, and we have found that the relationship which we found in the 0.02 carbon steel holds fairly well in other steels. For instance, in a series of ship plate steels, some of which were silicon-killed and some aluminum-killed, and normalized from different temperatures, we could plot transition temperature against ferrite grain size and find the same relationships or similar relationships to those reported in this paper. However, in those cases we would get a different line for each steel. The aluminum-killed steel would have a different transition temperature for a given ferrite grain size but the relation to the effect of ferrite grain size was the same.

In reply to Mr. Kramer, we have made no tensile tests on these steels. Neither have we done any double normalizing, but the effect of double normalizing would presumably be to give finer average ferrite grain and this presumably would have resulted in lower transition temperatures.

## Investigation of Temper Brittleness in Low-alloy Steels

by S. A. Herres and A. R. Elsea

DISCUSSION, W. M. Baldwin, Jr. presiding

I. R. KRAMER—It is usual in the study of temper embrittlement to heat treat specimens at temperatures in the region of 650°C and compare the results of the slowly cooling specimens with those of specimens which have been water quenched. Now often, especially in steels containing high percentages of manganese or nickel, there is a three-phase region in the neighborhood of these temperatures and there is a definite possibility of forming austenite during the tempering treatment. If the austenite is not stable it will decompose on slow cooling. However, in many cases it can be retained on quenching. The stability of the austenite will depend upon its composition, which in turn depends upon the base composition of the steel, the temperature, and the time the specimens are held at the temperature.

Whether or not the decomposition of the austenite formed during the tempering treatment embrittles the steel depends upon the temperature, or temperature range, at which it decomposes. In the work I have been able to do on this subject, it was found that on slow cooling the austenite could transform at rather high temperatures to form ferrite and pearlite. These decomposition products do not generally embrittle the steel to any great extent if the quantity of the decomposition products is not large. In other cases, the austenite will decompose at low temperatures to form

bainite or martensite. For this condition broad  $\alpha$  lines are generally found in the X-ray diffraction pattern and the specimens are greatly embrittled.

It was also found that in some cases the austenite which was retained at room temperature after either slow cooling or quenching from the tempering temperature could transform upon standing to embrittle the steel.

It is not my intent to explain all temper embrittlement phenomena by the formation and decomposition of austenite during the tempering cycle, but rather to point out that temper embrittlement may not be due only to one cause. I believe that in any study concerned with embrittlement as a result of tempering in the region of 650°C, care must be exercised to separate the effects of austenite formation and decomposition from other temper embrittlement phenomena.

A. R. ELSEA (authors' reply)—In this investigation, structural changes were followed by metallographic examination. The small amounts of austenite, referred to by Mr. Kramer, would be quite difficult to see under the microscope, especially if the austenite was finely divided and uniformly distributed. Probably, in work of this type, some other method of identifying small amounts of austenite should be used. However, in several cases, we determined the complete transition temperature curves for steels that differed only in phosphorus content. The effects of small amounts of austenite which might form during tempering should cancel out, unless the variation in phosphorus content influenced the amount of austenite which formed as the rate of its transformation.

L. D. JAFFE—In connection with Mr. Kramer's remarks about the possibility of austenite formation, Mr. Elsea mentioned that it is rather difficult to observe any austenite formation under the microscope with this kind of heat treatment. I am in complete accord with that statement, but there are other techniques available that are not so difficult. Mr. Kramer has mentioned dilatometric techniques. Another technique we have found useful is to apply the same treatment to a tensile bar and determine the yield-tensile ratio. If you get austenite formation even in amounts too small to be ordinarily found under the microscope, there is a very marked decrease in yield-tensile ratio, from the normal level of 0.8 or 0.9 down to perhaps 0.3.

J. A. KIES—I would like to point out that Hum, Parker and Hultgren of the University of California have recently studied temper brittleness in some high purity steels. They showed a number of Charpy impact energy vs. temperature curves for steels containing 0.20 pct carbon and various amounts of chromium. Temper brittleness was not detected for several compositions. One might assume from their report that it should be possible to make some steels free from temper brittleness, at least according to the current definition of the term.

I. R. KRAMER, *Materials Branch, Office of Naval Research, Washington, D. C.*; L. D. JAFFE, *Watertown Arsenal Laboratory, Watertown, Mass.*; J. A. KIES, *Naval Research Laboratory, Washington, D. C.*; C. T. HALLER, *Development and Research Division, International Nickel Co., Pittsburgh, Pa.*

C. T. HALLER—Would Mr. Elsea care to elaborate on the difference in the quenched microstructure of the steels containing 0.02 pct phosphorus as compared to those containing 0.005 pct phosphorus? I understand that the higher phosphorus steels contained no ferrite while the lower phosphorus steels contained a visible amount. This is of particular interest when one considers the alloy content of these steels and also the fact that they were brine quenched in a ½-in. section.

A. R. ELSEA—Hardenability curves were not determined for the steels used in this study and consequently we have no actual measure of the difference in hardenability resulting from the change in phosphorus content. We did observe a difference in the hardening pattern of the high and low phosphorus



steels which were water quenched from the austenitizing temperature. The low-phosphorus steels contained a small amount of ferrite. However, the specimens of the low-phosphorus steel used in this investigation were brine quenched, and in that condition no ferrite was observed.

## The Effects of Molybdenum and Commercial Ranges of Phosphorus upon the Toughness of 0.40 Pct Carbon Chromium Steels

by M. Baeyertz, W. F. Craig, Jr., and J. P. Sheehan

DISCUSSION, W. M. Baldwin, Jr. presiding

D. J. MACK—There are some apparently contradictory statements in the Discussion of Results. Near the end of the first paragraph, it reads: "Thus it seems reasonable to conclude that phosphorus reduced the toughness of the tempered martensite in the absence of temper brittleness." Then in the third paragraph: "The data obtained in this study substantiate the evidence presented by numerous investigators that phosphorus can cause temper brittleness in tempered martensite."

Conclusions 1 and 2 are similarly contradictory. A simple revision of these statements using the authors' definitions should eliminate the confusion.

D. J. MACK, Department of Metallurgical Engineering, University of Wisconsin, Madison, Wisc.

M. BAEYERTZ (authors' reply)—We are glad that Dr. Mack brought this question up, because the same point was raised in earlier informal discussions of the paper.

In stating that phosphorus reduced the toughness of tempered martensite in the absence of temper brittleness, we referred to the specimens that had been quenched in water after tempering at 1150°F. In this case raising the phosphorus content of 5140 from 0.020 to 0.036 pct raised the transition temperature about 40°F. It was assumed that this tempering treatment avoided temper embrittlement, and thus that the change in transition temperature was of a different nature than the embrittlement brought about by slow cooling after tempering at 1150°F. The latter was termed temper embrittlement in the paper.

## Discontinuous Crack Propagation—Further Studies

by L. D. Jaffe, E. L. Reed, and H. C. Mann

DISCUSSION, A. Smith presiding

G. R. IRWIN and J. A. KIES—Observations of microcracks associated with, but not directly connected to, the main path of fracture in steel were reported by Howe and Rosenhain nearly forty years ago. The recent work of Jaffe, Reed, and Mann, of Baeyertz, Craig, and Bumps, of Tipper, and of Ellinger and Williams have now shown rather convincing evidence that brittle fractures of steel are propagated by a discontinuous process. This opinion has been reached in the past by various workers from studies of the contours of fractured surfaces. Careful descriptive studies such as those given in this paper are and will continue to be of great importance in developing a satisfactory understanding of the fracturing process. At the Naval Research Laboratory we have tried to assist our understanding with model studies using a variety of materials. We have found that the level difference lines on fracture surface have systematic similarities in brittle fractures of metals and plastics and give us detailed information not only on the existence of discontinuities in fracturing but also on the manner in which these discontinuities develop. A paper by Kies, Sullivan and Irwin describes our work.

A point that may be of interest here is that our evidence for a discontinuous fracturing process seems to include ductile as well as brittle portions of mild steel fracturing. For segments of fracture which have relatively slow growth or which are accompanied by considerable plastic flowing, the apparent absence of side cracks does not rule out the possibility that such fracture segments grow by discontinuous propagation on a fine scale.

J. A. KIES—Fig. 14 is a picture by T. W. George taken originally at 30 diam, showing the main crack coming in from the left. It is in 2S aluminum foil five-thousandths of an inch thick. The foil is rather ductile and has been hanging under load for 30 days at room temperature. This proves beyond doubt that we have discontinuous fracturing even in a ductile



Fig. 14—Discontinuous crack in aluminum foil.

X30. Area reduced approximately three fourths in reproduction.

material. These holes opened up and were not connected with the main fracture.

Fig. 15 is a picture of what I like to call a parabola on a fracture in very ductile fine-grain tempered steel. This was furnished by W. J. Harris, Naval Research Laboratory, Metallurgy Division. It shows the nucleus. We do not know the nature of the flaw or whatever it was that initiated the crack. There is a sheared wall, conical in nature, in that pit. That pit is a good deal like one we saw showing a parabola developed on the fractured surface of lucite. This can be found over and over again on ductile fractures of steel. If one looks in the microscope at the sheared walls on ductile failures one can see the sort of thing that appears in the focus of the parabola. This occurs on an extremely fine scale.

Fig. 16 is our model fracture showing the way herringbone or chevron markings on ship plate are made. One can see an individual fractured element nucleated primarily near the center of the plate. This happens to be a plate of cellulose acetate. It consists of separated nucleated fractures. Here we see the focal pits connected with each separated portion. The

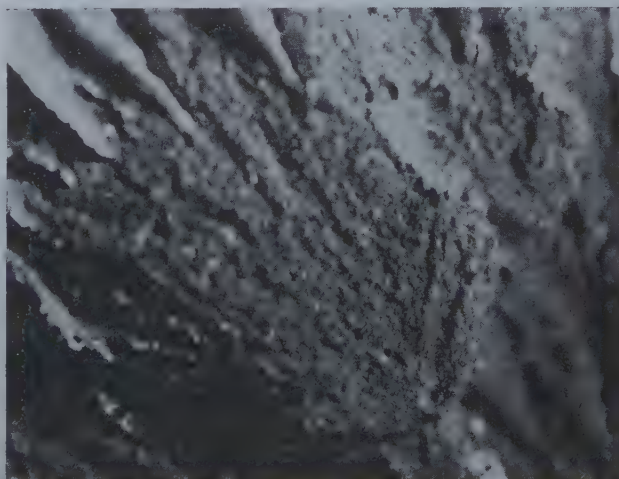
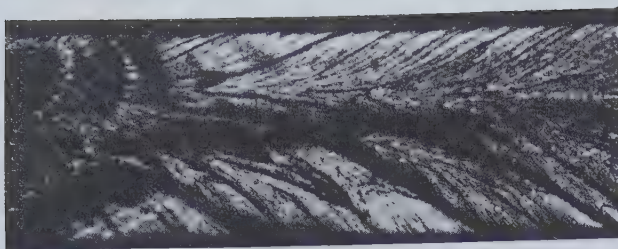


Fig. 15—Fracture in very ductile tempered steel.





**Fig. 16—Cellulose acetate fracture showing the formation of herringbone markings.**

X100. Area reduced approximately three fourths in reproduction.

fractures go toward the right. The fact that they are on different levels makes the lines between them form the herringbone markings.

We are willing to go out on the limb even further than Dr. Jaffe and suggest that all fractures, even ductile ones, are primarily and essentially discontinuous.

G. R. IRWIN and J. A. KIES, *Mechanics Division, Naval Research Laboratory, Washington, D. C.*; W. H. BRUCKNER, *Department of Metallurgical Engineering, University of Illinois, Urbana, Ill.*; A. MONTGOMERY, *Aluminum Co. of America, Cleveland, Ohio.*; A. G. GUY, *North Carolina State College, Raleigh, N. C.*; M. BAEYERTZ, *Armour Research Foundation, Chicago, Ill.*

L. D. JAFFE, E. L. REED, and H. C. MANN (authors' reply)—We are interested in this work of Dr. Kies and Dr. Irwin. It has long been known that ductile discontinuous fracture occurs in the case of high-temperature grain boundary failures of metals. The fracture in the aluminum foil (fig. 14) may be a grain boundary fracture rather than a fracture through grains.

J. A. KIES—Perhaps you are right in this case. We find the same thing in fast fracture of the foils and in all cases straight portions of the cracks are much longer than the grain size. Ductile action precedes the opening of the slow ones and it is difficult to determine whether the crack is transgranular or not. Grains are then indefinite.

L. D. JAFFE, E. L. REED, and H. C. MANN—Discontinuous grain boundary fracture is common in alloys at fairly high temperatures, and aluminum at room temperature under very slow straining might also develop a series of cracks that progress from one grain boundary to another. Thus Dr. Kies gets cracks much larger than a single grain, but along grain boundaries, whereas Baeyertz, Craig, and Bumps, and our group have been studying fractures through the grains.

It is interesting to relate the failures in plastics and other materials, such as glass, to those in metals. However, we are concerned here with propagation of a crack from one grain of a polycrystalline metal to another, and an amorphous glass would not have anything corresponding to that. We are wondering whether plastics would have.

W. H. BRUCKNER—I was very much interested in this paper in which the authors have stated that it was not possible to determine whether the twin nucleated the cleavage crack or whether the cleavage crack nucleated the twin. I have obtained a micrograph of a single ferrite grain in which there are three twins and a cleavage crack crosses all three twins. Along the cleavage crack the three twins have translated showing the cleavage crack as a faulting plane, thus indicating that the twins form first and cleavage follows.

A. MONTGOMERY—I should like to know if the authors investigated to prove positively that the secondary cracks were discontinuous. The micrographs show the microcracks all closely associated with the main failure. Is it impossible that they are merely secondary branches connected to the main fracture in some other plane? Possibly the authors followed them by successive polishing and examination to prove they were discontinuous.

L. D. JAFFE, E. L. REED, and H. C. MANN—That is a very important question. We are in the process of polishing down through some of these cracks to ascertain definitely whether or not they are connected in the third dimension. Also, at the suggestion of Dr. Kies, we have studied the fracture of sheet, only one grain thick, where you would not expect the third dimension to contain any linking up. We have found in such material discontinuous cracks.

A. G. GUY—The question I have concerns the Neumann bands. I believe those are twins and if they are twins they should not disappear on further polishing. It seems strange that their direction should coincide with the direction of cracking although I believe that crystallographically you might account for that under some special circumstances. Will you comment on whether your Neumann bands did disappear on further polishing?

L. D. JAFFE, E. L. REED, and H. C. MANN—The twins disappear on repolishing, as would be expected. If the repolishing is followed by re-etching, they reappear. Presumably this is what Dr. Guy had in mind.

M. BAEYERTZ—It is interesting to hear of work that describes just about the same sort of cleavage as we have been observing in the brittle portions of fractures, but in a steel that was heat treated in an entirely different way, as Dr. Jaffe's steel was. Our steel had a pearlitic structure; however, the cleavages in the fractures appear to be similar in the two cases.

L. D. JAFFE, E. L. REED, and H. C. MANN—After presentation of our paper, we found an additional reference<sup>13</sup> along similar lines.

<sup>13</sup> E. Shevandin: The Spreading of a Brittle Fracture Crack. *Tech. Phys. U.S.S.R.* (1938) 5, 279-288.

## Stress and Strain States in Elliptical Bulges

by C. C. Chow, A. W. Dana, and G. Sachs

DISCUSSION, A. Smith presiding

W. T. LANKFORD—What was the size of opening over which the bulges were formed? The ratio of the size of the opening to the thickness of the sheet must be quite high to meet the thin shell conditions assumed in the stress calculations. Did the authors consider the direct calculation of stresses in elliptical bulges? If the deformed membrane conforms quite closely to a surface of revolution about a horizontal axis parallel to the major axis of the elliptical opening, the stresses can be calculated from the pressure, the sheet thickness and the principal radii of curvature, using eq 1. Fig. 3 indicates that the material was substantially isotropic, but the experimental points lie somewhat below the line of complete isotropy. L. R. Jackson, K. F. Smith and myself<sup>12</sup> have presented a theory for

<sup>12</sup> L. R. Jackson, K. F. Smith, and W. T. Lankford: Plastic Flow in Anisotropic Sheet Steel. *Trans. AIME* (1949) 180, 415; *Met. Tech.* (Aug. 1948) TP 2440 E.

the type of anisotropy found in rolled sheet. Did the authors apply this theory to attempt to account for the experimental deviations from the theory of isotropic materials?

A. W. DANA (authors' reply)—I should mention that this work was originally done two years ago and since that time considerable interest has been shown in bulges, as Dr. Lankford pointed out. The work on which the paper was based has not been carried further, as far as I know, and therefore, some of the points in Dr. Lankford's discussion have not been checked. In regard to the geometrical conditions for solving stresses in the bulges, at the time this work was initiated, we made an attempt to calculate the stresses on this basis. It was found that inaccurate

W. T. LANKFORD, *Carnegie-Illinois Steel Corp., Pittsburgh, Pa.*



results were obtained and for that reason we went over to stress-strain relations.

The circular bulge was 6 in. in diameter. The small ellipse was 6 in. long, and 4 in. wide, bead shape was 12 in. by approximately 4.

## The Comparative Creep Properties of Several Types of Commercial Coppers

by A. D. Schwope, K. F. Smith, and L. R. Jackson

DISCUSSION, H. P. Croft presiding

D. L. MARTIN—The authors give results which indicate that OFHC copper is better in "creep" than tough pitch copper, and also show in fig. 8 that the secondary creep rate of OFHC at 300°C is lower than for tough pitch copper containing 25 oz. silver per ton.

On the other hand, rupture tests at 200°C by other investigators have shown tough pitch copper to be similar to OFHC, and silver-bearing tough pitch copper to be stronger than OFHC copper.<sup>3</sup> This is in

<sup>3</sup>D. L. Martin and E. R. Parker: Effect of Cooling Rate and Minor Constituents on the Rupture Properties of Copper at 200°C. *Trans. AIME* (1944) 156, 126.

agreement with the work by Burghoff and Blank already mentioned by the authors.

In view of the higher cost of OFHC copper over tough pitch, and of silver-bearing grades over regular grades it is important that the relative strength characteristics be properly evaluated. I hope the authors will continue their work on these coppers at lower temperatures and lower stresses (e.g. "creep" at 25,000 psi is meaningless for commercial purposes).

D. H. WOODARD—Was the dead weight loading applied in one unit or in increments?

Results on Monel metal which had been tested in creep below the recrystallization range show that prior extension increases the resistance to creep. The second-stage rate is also a function of the rate of loading.

D. L. MARTIN, *Research Laboratory, General Electric Co., Schenectady, N. Y.*; D. H. WOODARD, *National Bureau of Standards, Washington, D. C.*

A. D. SCHWOPE (authors' reply)—It is to be pointed out that in their paper, Messrs. Martin and Parker present data definitely showing OFHC copper to have rupture properties superior to those of tough pitch copper. Also, the longer lifetime found for the silver-bearing tough pitch was attributed to its relatively finer grain size, one-sixth that of the OFHC coppers. In view of these considerations, the apparent inconsistencies between results are eliminated.

In reply to Mr. Woodard, the load was applied in one unit or as nearly so as possible. As an example, if the load consisted of two 50-lb weights, these were loaded individually as rapidly as possible.

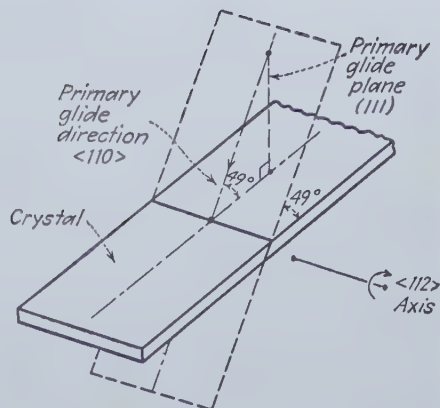
## The Active Slip Systems in the Simple Axial Extension of Single Crystalline Alpha Brass

by R. Maddin, C. H. Mathewson, and W. R. Hibbard, Jr.

DISCUSSION, H. P. Croft presiding

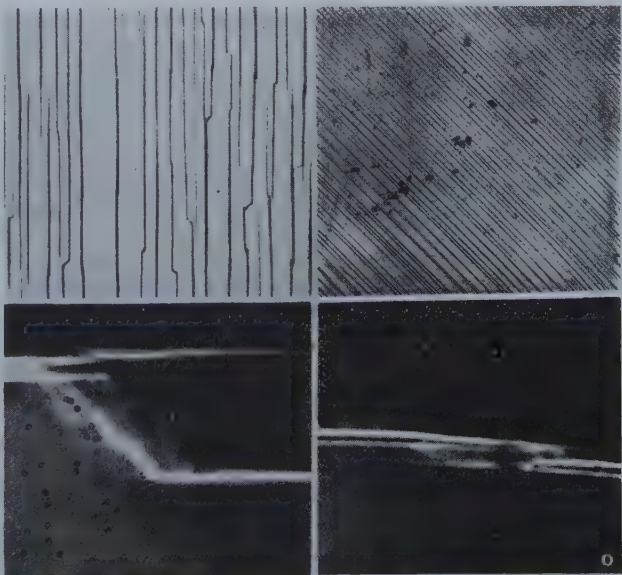
R. W. CAHN—I have been much interested in this paper and its predecessor, particularly as I have recently had occasion to study in single crystals of aluminum a phenomenon similar to the cross-slip described by the authors. The crystals were ribbon-shaped and of predetermined orientation, as shown in fig. 23. Observations were made on two electrolytically polished flats parallel to the crystal axis, one parallel to the plane of the ribbon and one perpendicular to it. It may be mentioned, in view of the

Fig. 23—Orientations of aluminum crystals.



authors' interest in lattice rotation, that the glide direction, the normal to the glide plane and the crystal axis were coplanar, a situation not met in the general case and which entails that rotation about the one  $\langle 112 \rangle$  axis marked suffices to accommodate entirely the lattice rotation near the grips.

Fig. 24 shows the appearance of the wide surface of a crystal extended by 7 pct (shear 0.14). A good deal of cross-slip can be seen, and it is to be noted that the cross-slip takes place on several different planes. In no case did the narrow surface show any sign of cross-slip, as may be seen from fig. 25. Since this surface was approximately parallel to the operative primary glide direction, it follows that glide on all the cross-slip planes took place parallel to this same, common  $\langle 110 \rangle$  direction. An analysis of numerous cross-slip traces showed that (111), (100), and (212) were the most common; several other planes probably also took part. A good analogy to the nature of slip in these crystals may be found in the motion of the saddle over the bed of a lathe. The cross-slip traces were not generally dead straight and certainly their directions were not as well defined as in the authors' beautiful micrographs; this was due to the fact that (as Heidenreich and Shockley<sup>3</sup> have shown) the slip-lines actually consist of numerous fine lines not normally resolved by the optical microscope, and these undergo cross-slip in a complicated way. Fig. 26, taken at maximum magnification, shows an example; the separate fine traces are just resolved here because they are spread out more in the region where cross-slip takes place. It was also found that the places, often seen in low-power micrographs, where neighboring slip-



Figs. 24-27—Crystal stretched as follows:

Fig. 24, 7 pct wide surface, X310; fig. 25, 7 pct narrow surface, X180; fig. 26, 5 pct wide surface, X2350; fig. 27, 5 pct wide surface, X2350. Area reduced approximately one ninth in reproduction.



lines fade out opposite each other, are sites of what the authors have called *intimate* cross-slip; the fine slip-lines undergo cross-slip one behind the other over a considerable distance, so that the individual cross-slip traces are too fine to be seen at low power. This may be seen in fig. 27.

A small amount of slip on the conjugate system preceded and accompanied the primary slip on some parts of the specimens; oddly enough, the conjugate slip-lines revealed no cross-slip at all, in contrast to the authors' observation with brass.

In connection with the cause of cross-slip, the following observation is of interest. A crystal of the orientation already mentioned was bent about the transverse axis lying in the plane of the ribbon (this axis was the  $\langle 112 \rangle$  direction perpendicular to the glide direction, and lying in the glide plane). Such *pure bending* gave rise to a relatively small amount of cross-slip. A crystal bent accidentally into a slightly skew shape (i.e. not exactly about any one axis) exhibited much more cross-slip. The authors' general view that cross-slip is in some way correlated with inhomogeneous deformation is supported by this; yet it is hard to see just what this correlation means, for the occurrence of cross-slip as described is quite compatible with perfectly homogeneous deformation. Examination of the slip lines, near the grips, on extended aluminum crystals showed that cross-slip did not to any large extent replace *flexural glide*. The authors have reported that up to a certain shear there is, with brass crystals, little or no Laue asterism (and therefore little lattice curvature or inhomogeneity of deformation). Since even a small shear sufficed to bring about cross-slip, it is evident that inhomogeneity of deformation is not a necessary precondition for cross-slip to occur. With aluminum, it has been possible to show that asterism is almost entirely due to deformation bands which are a form of highly localized *flexural glide*. Since these bands occupy only a small fraction of the crystal while cross-slip takes place everywhere, it is perhaps not surprising that asterism and cross-slip are not correlated.

It is probable that cross-slip will prove to be explainable in terms of dislocations. The characteristic property of an edge dislocation line is the vector parallel to the glide direction; there is no theoretical objection to the dislocation line itself being stepped. If it is, then it will sweep out a stepped glide zone made up of two or more glide planes. Why a dislocation line should become stepped at one point rather than another remains, for the moment, a mystery; but it does seem probable, in view of the bending experiment and of the lack of cross-slip in the conjugate slip planes which precede primary slip, that the stepping is created as a consequence of preceding deformation (as the authors suggest), and is not an original property of the dislocations.

A point which ought perhaps to be borne in mind when one seeks to explain this phenomenon is that it appears to be restricted to cubic metals. Hexagonal metals exhibit neither cross-slip nor deformation bands.

The experiments referred to above are in course of publication.

R. W. CAHN, Ministry of Supply, Atomic Energy Research Establishment, Harwell, England.

C. H. MATHEWSON (authors' reply)—Mr. Cahn's work on aluminum crystals is especially welcome as a collateral contribution of well documented data which are needed in considerable variety to clarify the interrelationships of stress and strain in the general process of plastic deformation. His observation that cross-slip in aluminum often parallels other planes than the octahedral plane observed in Maddin's experiments on brass has been confirmed in this laboratory. Rosi,<sup>20</sup> Rosi and Mathewson,<sup>21</sup> show one case in which the cross-slip could be resolved into segmented slips parallel to

the primary slip plane and the usual cross-slip plane. Possibly the markings observed by Cahn have resulted from cooperative slip of this character, as indeed his fig. 26 suggests. It is especially interesting to note that cross-slip can be observed as connecting segments in many places where neighboring slip lines seem to fade out.

The writer believes that cross-slip is produced by shear stresses across the glide lamellae arising from the twisting distortion accompanying slip at the boundaries. This is based on the assumption of a resolved stress acting as a driving force in the close-packed direction  $\langle 110 \rangle$  which, owing to lattice constraint, produces movement in a sidewise direction  $\langle 112 \rangle$ . On this basis there is inhomogeneous deformation in the neighborhood of every slip site. In the writer's view the absence of asterism in an early stage of deformation merely indicates that the inhomogeneity of deformation which would produce it has been modified by cross-slip.

It is agreed that cross-slip "does not replace flexural glide." Again, it is probable that confirmation of many observations made by Cahn on deformation bands and flexural glide may be found in recent work from the Hammond Laboratory.

Thus Neng-Kuan Chen<sup>22</sup> has made a careful study of deformation bands in crystals of many orientations. Most crystals produce bands, but there is an area of orientation spreading out from the  $\langle 111 \rangle$  pole of the Taylor and Elam triangle in which flexural gliding seems not to occur and the deformational behavior resembles that of brass. The writer believes that in such cases the function of flexural gliding is replaced by slip across the glide lamellae on planes of the conjugate family. There is a further similarity with brass in that slip bands are much more irregularly spaced in such orientations, assuming a strongly clustered appearance.

With respect to dislocations, the writer takes the position that it is more profitable to look for explanations of slip phenomena in terms of a more conventional crystal mechanics than primarily on the basis of fault propagation or other attributes of dislocation theory. In this sense, dislocations, perhaps more mildly termed displacements, are regarded as the consequence and not the cause of changes in the crystal accompanying an overall forced change in shape.

With respect to deformation bands, in the Hammond Laboratory we emphasize the point that the "bend planes" observed as early as 1934 by R. F. Miller<sup>23</sup> are the locus of the axes around which the slip planes bend in this modification of simple flexural gliding. A pair of bend planes thus defines a band in which the reorientation lags behind that of the matrix material in the process of axial extension. Miller observed bend planes but no bands, but the writer has seen deformation bands in many zinc crystals. They have not been observed in the numbers of experiments with copper and brass performed in this laboratory. In Chen's aluminum crystals, the slip direction constituted the pole of the band, and the axis around which the slip direction changed its orientation was the intersection of the glide ellipse with the band ellipse, namely,  $\langle 112 \rangle$ .

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# Simultaneous Aging and Deformation in Metals

by J. D. Lubahn

DISCUSSION, E. H. Hollingsworth presiding

G. A. MOORE—This discussion is by proxy. Mr. H. B. Gayley of our laboratory did some work on the natural stress-strain curves of 24S last spring, and he has requested that the information on this discontinuous flow be amplified by including some of his observations.

In summary, on tests of 24S alloy, the discontinuous flow was obtained only on specimens which were actually in process of aging during the test. Discontinuous flow was observed on specimens immediately after quenching from the solution anneal to room temperature and throughout the aging period.

G. A. MOORE, *Department of Metallurgy, University of Pennsylvania, Philadelphia, Pa.*

After aging was completed, discontinuous flow was not observed and it was not observed in specimens which had been partially aged at elevated temperature and tested at room temperature. According to the limited number of tests made, aging for 10 min at 60°C or higher apparently was sufficient to eliminate the effect in this alloy.

J. D. LUBAHN (author's reply)—It is not at all surprising to find the effect Mr. Moore described in 24S. As a matter of fact, the more metals that we test and the more conditions under which we test them, the more it becomes apparent that nearly all metals show some of the phenomena described in the paper (at least under one circumstance or another).

I would like to make a comment, too, about the observation that discontinuous yielding only occurred while the 24S was aging. It seemed that way from our experiments, too. Fig. 1 shows that when the aging time was short (so that the aging would have been rapid) discontinuous yielding was observed. On the contrary, after a long time of aging, when the rate of aging would have decreased to a considerably smaller value, the phenomenon did not appear. Thus, if the aging is going to have an effect on the deformation, it must be going on at a sufficiently fast rate. Of course, the rate of the deformation would have an effect; if an experiment were made just on the borderline between continuous and discontinuous yielding and if the strain rate were changed in one direction or another, the phenomenon could be made to appear or disappear.

## The Transverse Bending of Single Crystals of Aluminum

by M. K. Yen and W. R. Hibbard, Jr.

DISCUSSION, E. H. Hollingsworth presiding

B. R. BANERJEE—It is desirable not to associate these traces of cracks in an oxide film of doubtful crystallographic nature with the term "strain markings," a standard term of crystallographic significance used to describe a metallographic phenomenon associated with plastic deformation.

B. R. BANERJEE, *Department of Metallurgical Engineering, Illinois Institute of Technology, Chicago, Ill.*; R. W. K. HONEYCOMBE, *Cavendish Laboratory, Cambridge, England.*; E. A. CALNAN, *National Physical Laboratory, Teddington, England.*

R. W. K. HONEYCOMBE—The results recorded in this paper are very interesting, in particular I would like to refer to the X-ray observations. I have been studying the asterisms resulting from slightly deformed aluminum single crystals and have found in

all cases a fine structure similar to that observed by the authors. The Laue spots became multiple after as little as 1 pct elongation in tension. Further deformation ultimately caused the spots to merge into the continuous background of the asterism. The number of intensity maxima increased as the size of the X-ray beam increased, and in fact if a very fine beam were used, sometimes no fine structure was detected.

I do not think that this phenomenon is due to polygonization as described by Cahn,<sup>26</sup> because polygonization usually occurs during annealing of deformed single crystals at high temperatures (300°C or higher for aluminum). Furthermore, my experiments with aluminum crystals have shown that polygonization results in a marked decrease in the yield point, whereas the other phenomenon has no such effect, and is in fact evident immediately deformation has occurred at room temperature.

The cause of this room temperature "fragmentation" can, I think, be seen in one of the authors' own photographs (fig. 6) in which they show narrow bands which are only visible in oblique illumination. I have also observed these narrow bands in large aluminum crystals deformed in tension (fig. 24), and am of the opinion that they are narrow deformation bands or kinks. It seems that plastic deformation does result in the "fragmentation" of the crystal into narrow blocks within which slip occurs normally. The boundaries between the blocks, namely the deformation bands, are regions of abrupt changes in orientation in the form of local curvatures, although these local curvatures are larger than those postulated by Burgers and Taylor. It is suggested that the maxima in the Laue asterisms result from these blocks while the continuous background arises from the deformation bands.

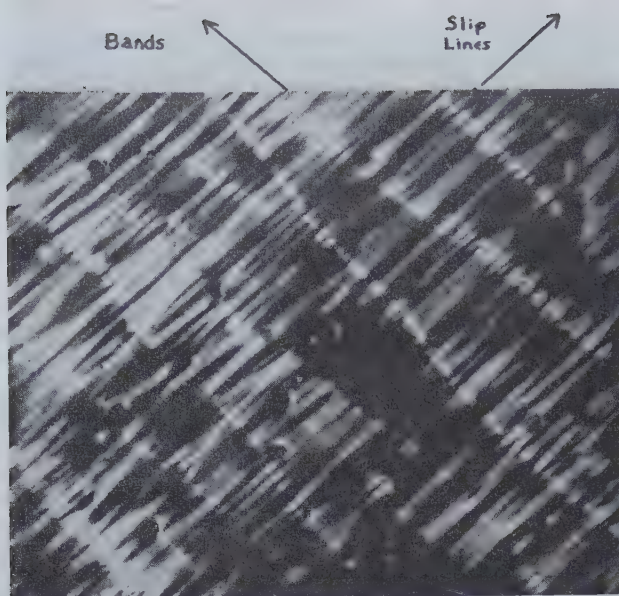
This hypothesis has been confirmed by the writer recently, using an X-ray technique similar to that described by Berg<sup>27</sup> and Barrett,<sup>28</sup> in which a monochromatic X-ray beam from a line focus is reflected from a crystal. The technique has been used to examine large aluminum single crystals which have been slightly deformed in tension (1 to 5 pct elongation); the crystal is rotated until a strong reflection is seen on a fluorescent screen. The screen is then replaced by a Kodak Maximum Resolution Plate which is placed within 3 mm of the surface of the crystal. The resulting image has a fine structure which when examined at high magnification (X30 to X100) in a microscope, reveals a pattern which is in effect a map of the changes in orientation in the crystal. A deformed crystal gives a network of bands (figs. 25 and 26), which do not correspond with the slip lines but cross them, and it is now clear that they represent the deformation bands visible only with difficulty in the optical microscope.

By obtaining reflections from two surfaces at right angles and correcting for angular distortions on the photographic plate, it has been possible to determine the plane of the bands. In the cases so far examined, the bands form on (110) planes. The spacing between the bands is about 0.04 to 0.08 mm while their width is considerably less (0.005 mm). However, in polycrystals, or in single crystals near small included grains, the bands become much larger and more clearly defined.

Thus it appears that in single crystals of aluminum even in the very early stages of plastic deformation (0.75 pct elongation), slip is accompanied by deformation bands or kinks which are the cause of the effects observed in X-ray Laue photographs. It is interesting to compare the behavior of hexagonal metals. The writer has shown that cadmium crystals can be extended to as much as 100 pct elongation without the occurrence of asterism. Examination by the Berg-Barrett X-ray method shows that deformation bands are absent in cadmium crystals after 20 pct elongation in tension.



24



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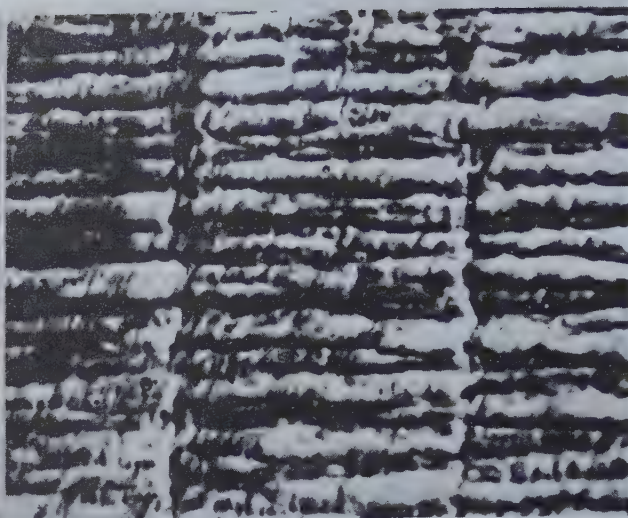


Fig. 24—Aluminum crystal. 10 pct elongation. Micrograph taken in oblique illumination. X200. Fig. 25—Berg-Barrett X-ray micrograph of an aluminum crystal after 4 pct extension showing deformation bands. X50.

Figs. 24-25. Area reduced approximately one seventh in reproduction.

E. A. CALNAN—In an investigation of creep in aluminum now being completed at the National Physical Laboratory some time has been devoted to the analysis of distorted Laue spots in back-reflection patterns. Observations were made on various parts of individual grains in a polycrystalline testpiece after various amounts of slow creep extension at 250°C. Up to approximately 3 pct extension, patterns very similar to those shown by the authors were found. In this range one grain exhibited simple elongation of the Laue spot similar to figs. 16 and 17 and the lattice rotation appeared to be in the single crystal direction, i.e., the stress axis moved towards the opposite  $[110]$ . It was considered that the direction of the spread of the spot could be due to crystallite rotation about an axis in the slip plane perpendicular to the slip direction, as found by Taylor and other workers, but it might equally well be due to inhomogeneous single crystal rotation, i.e., rotation about an axis perpendicular to the stress axis and the slip direction, for these two axes were quite close.

From the stress axis orientations for specimens A-10, A-11 and A-15 shown in fig. 4 and the patterns in figs. 16 and 17, it would seem doubtful whether the aster-

ism can be attributed to rotation about the axis in the slip plane rather than to inhomogeneous single crystal rotation. It should be possible to differentiate between the two when the stress axis is near the  $[100]$  or  $[111]$  directions and it would be interesting to know if specimen A-2 throws any light on this point.

In other grains we have observed splitting and elongation of the spots, similar to figs. 18 and 19, and the general lattice rotation did not appear to agree with the single crystal direction. In adjacent parts of the same grain the directions of splitting were quite different, suggesting that there was a substructure of areas of different rotations which may be due to Taylor crystallite rotation, to inhomogeneous single crystal rotation, or to rotation about the slip plane normal suggested by the authors. The size of the substructure at this stage would appear to be a fraction of the area irradiated, in this case 0.4 mm diam.

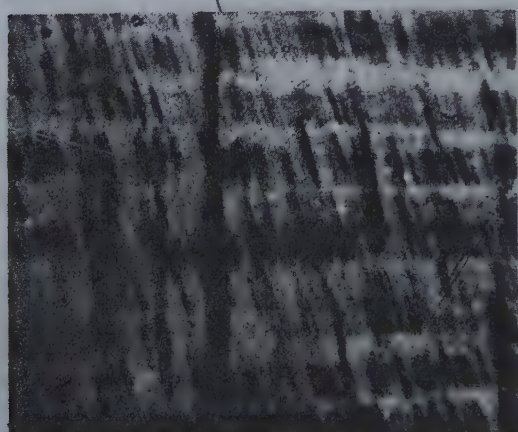
M. K. YEN and W. R. HIBBARD, JR. (authors' reply)—The authors wish to thank Messrs. Honeycombe and Calnan for their interesting comments. In regard to the deformation bands described by Mr. Honeycombe, recent work by N. K. Chen in Hammond Laboratory, Yale University, also showed that in extended aluminum single crystals, the deformation bands form on the  $(111)$  plane, the pole of which coincides with the acting slip direction. However, the formation of the bands appeared to be orientation dependent. Crystals having their axes near  $[110]$  did not produce bands.

The Laue spots on X-ray photograms for specimen A-2 have been examined. Unfortunately, the specimen was used for our preliminary work and X-ray photograms were taken only on the compression side. The asterism is only slight but it does not conform to the inhomogeneous single crystal rotation described by Mr. Calnan. In view of results reported by Hibbard<sup>29</sup> that orientation within the individual grain in polycrystalline specimens are rather dispersed due to strain heterogeneities caused by grain boundaries, it would not be expected that the results obtained from polycrystalline and single crystal specimens would be similar.

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- <sup>28</sup> C. S. Barrett: *Trans. AIME* (1945) 161, 15.
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Slip  
Lines



Deformation  
Bands

Fig. 26—Berg-Barrett X-ray micrograph of an aluminum crystal (4 pct elongation) showing slip band lines crossing deformation bands.

X50. Area reduced approximately one ninth in reproduction.



# Stages in the Deformation of Monel Metal as Shown by Polarized Light

by D. H. Woodard

DISCUSSION, L. D. Jaffe presiding

B. R. BANERJEE—While this method of examination seems to be extremely useful in the study of plastic deformation and the formation of deformation bands, it should not be overlooked that the bending and waviness of the slip lines as observed here are a very gross effect compared to the much smaller scale of the fundamental irregularities, faults, and fragmentation of the crystals. If, for example, these "wavy" slip lines were due to slip occurring on planes cutting across other sets containing twin faults as suggested by Barrett,<sup>14</sup> or due to slip on planes passing through domains of slightly differing orientations of the type recently referred to by Heidenreich,<sup>15</sup> the present method of observation would certainly be unable to resolve them.

Dr. Woodard has concluded "initial plastic deformation occurs through the bending of the lattice around a single axis," but as Mathewson et al.<sup>16</sup> have shown that even in single crystals (with favorable orientations for slip on a single slip system) three slip systems are operative from the very beginning. The stress distribution in a polycrystalline material is much more complex and one would hardly expect either slip or bending to be of such a simple and uniform nature. In the opinion of this writer, in interpreting the results, the mechanism of deformation of a polycrystalline material has been over simplified, completely ignoring the effects of fragmentation which is now known to occur on an order of 200 to 800 Å (the so-called granular details of Heidenreich<sup>15</sup>) as well as the classical domains of the order of magnitude of  $10^{-4}$  cm.

D. H. WOODARD (author's reply)—As Dr. Banerjee has pointed out, the observations described in this paper are of microscopic order of magnitude. The possibility does exist that cross-slip and/or rotations of the fragmented lattice can cause the curving of the slip lines. Yet, the smoothness of the lines at magnifications of X2000 and the fact that slip lines were observed whose curvature was parallel to and similar to that of deformed twin interfaces (they are both traces of the octahedral planes) lead me to feel that they represent bendings of the planes of maximum density. Twin faults, if they are created in Monel dur-

ing slight deformation, should not be likely to give such a regularity of pattern. As Dr. Barrett has pointed out, the extreme irregularity and waviness of slip lines of highly deformed Monel might be caused by faulting. When creep specimens of Monel are loaded in increments so small that there is no resultant lattice bending, minute aligned areas of different orientation are observed lying parallel to the twin interfaces. These I like to think of as representing areas of rotated crystallites. (Unpublished work.)

R. MADDIN—I should like to call attention to a slightly different interpretation of some of the very interesting data presented in this paper. The author shows (fig. 2) that rotation of the plane of polarization results in a change in intensity from the one grain to the next. It is also apparent from fig. 2 that the intensity change between twins and their matrix grain is not always so noticeable as between neighboring grains. Consequently, it seems quite possible that what the author terms as bent lattice structure may be slip across many annealing twins since some of the author's micrographs, fig. 5, b, c and fig. 6 give strong indication of containing ponderable twins. The slip lines shown in the large grain in fig. 5c, for example, are similar to the slip lines appearing in a recrystallized copper or brass specimen which has been slightly strained, i.e., they are parallel on both sides of the twin. Again in fig. 6, the slip lines appear as if they have passed through a series of annealing twins.

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D. H. WOODARD—Although there are many unabsorbed twin orientations that exist in annealed Monel, one has always been able to observe the differences in orientation under polarized light. The straight twin interfaces, which would be severely distorted by the time deformation bands were formed, were not observed as delineating those bands. Under such circumstances, I do not feel that the changes in direction of the slip lines can be wholly attributed to their passage through annealing twins.

W. R. HIBBARD, JR.—I suggest that this technique be evaluated by the use of single crystals with a simple mode of deformation where the exact changes in struc-



7

Fig. 7—Uranium bar with plane of polarization rotated 70°.

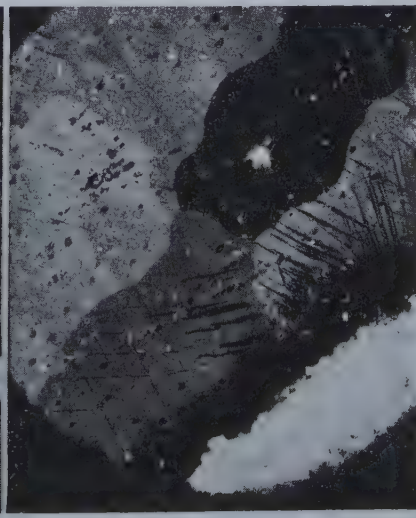
X100. Polarized light. Area reduced approximately three fourths in reproduction.



8

Fig. 8—Same as fig. 7 with plane rotated 90°.

X100. Polarized. Area reduced approximately three fourths in reproduction.



9

Fig. 9—Same as fig. 7 with plane rotated 110°.

X100. Polarized light. Area reduced approximately three fourths in reproduction.





**Figs. 10-11—Zirconium bar reduced 96 pct by cold-swaging.**

Fig. 10, Transverse. X50. Polarized light. Fig. 11, Longitudinal. X100. Polarized. Area reduced approximately one fourth.

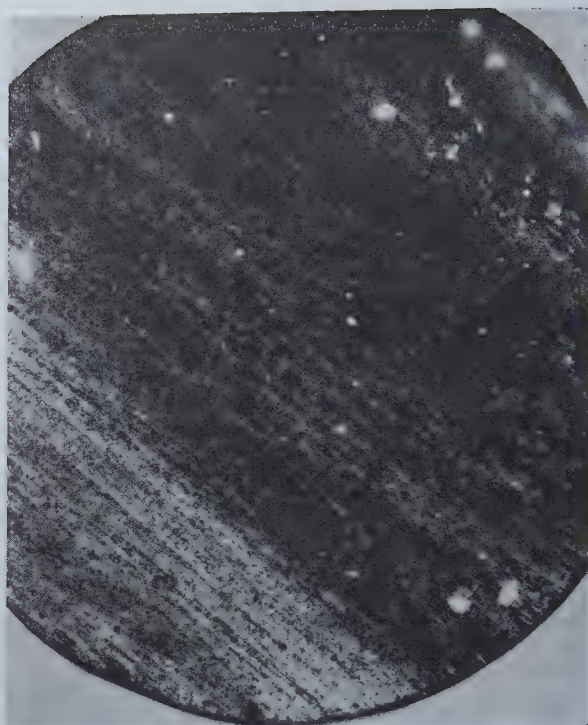
ture, orientation, and so forth, can be measured by other means such as etch pits and X-ray, and then the sensitivity of polarized light microscopy determined accurately.

R. M. TRECO—In my work for the atomic energy program, it has been necessary to use polarized light for several years as a standard metallographic method for analyzing the microstructures of rather unusual metals. The method has proved quite satisfactory for such metals as beryllium, zirconium, uranium, etc. in the cold-worked, annealed, and heat-treated stages. Polarized light is very sensitive to variations in crystallographic orientation in different grains and in the substructure within a single grain. Figs. 7, 8, and 9 show the microstructure of a uranium bar with the plane of polarization rotated  $70^\circ$ ,  $90^\circ$  and  $110^\circ$  respectively, to show the presence of intersecting twin bands. It will be noted that the  $90^\circ$  rotation corresponding to crossed nicols is the correct angle for interpretation of the microstructure, since a maximum of detail is present. Samples such as this, electropolished only, show no detail under bright light, and the presence of an oxide film of the order of 200 Å in thickness does not affect the structure obtained.

Dr. Woodard has shown us the early and intermediate stages of cold working only. It is interesting to consider also the effects of much heavier deformations, figs. 10 and 11 showing the transverse and longitudinal structures respectively of crystal bar zirconium cold-swaged to a reduction of 96 pct. The light areas in the transverse section indicate a high degree of preferred orientation.

By examining the longitudinal section of the same specimen we effectively rotate the plane of polarization through a  $90^\circ$  angle and find that the bright areas of the transverse section now appear as dark longitudinal bands, while the formerly dark areas are light bands which remain dark through a complete rotation of the stage. The microstructure of cold-worked zirconium thus shows an unusual type of fibering under polarized light and indicates a strong preferred orientation around the longitudinal axis of the bar.

D. H. WOODARD—I would like to thank Dr. Hibbard and Mr. Treco for their encouraging remarks. The micrographs of Mr. Treco show areas which are apparently deformation twins. Somewhat similar areas have been observed in Monel specimens that have been fractured in liquid nitrogen. A study of the development of preferred orientation, as shown by polarized light, is now in progress and will be reported shortly. As Mr. Treco has shown, both uranium and zirconium are optically anisotropic.



### References

- <sup>14</sup> C. S. Barrett: Twinning and Banding. *Trans. A.S.M.* (1949) 41A.
- <sup>15</sup> R. D. Heidenreich: Structure of Slip Bands and Cold Worked Metals. *Trans. A.S.M.* (1949) 41A.
- <sup>16</sup> R. Maddin, C. H. Matthewson, and W. R. Hibbard, Jr.: The Active Slip Systems in the Simple Axial Extensions of Single Crystalline Alpha Brass. *Trans. AIME*, 185, 527; *Jnl. Met.* (Aug. 1949) TP 2658E.

## Influence of Temperature on the Stress-strain-energy Relationship for Copper and Nickel-copper Alloy

by D. J. McAdam, Jr.

DISCUSSION, L. D. Jaffe presiding

G. W. GEIL—Dr. McAdam has presented many thought provoking ideas in this paper. The numerous assumptions and the novel method of developing a stress-strain-energy relationship for metals may present a qualitative picture of this relationship.

The procedure and assumptions used by the author for deriving flow-stress curves from experimental data obtained at the National Bureau of Standards on Monel and copper, as tested in tension at various temperatures, are given in some detail in the text. At the time these tests were made, no suitable method was available for following the change in diameter of the specimens during the tests at subzero temperatures. Thus the procedure used by the author in deriving the flow-stress curves was perhaps the best available to him. However, subsequent to Dr. McAdam's retirement from this Bureau in 1947, tension tests at subzero temperatures have been made on Monel and other metals in which changes in diameter were accurately followed during the entire test. Flow-stress curves as established from such measurements on specimens of the same heat of annealed Monel tested at  $-188^\circ\text{C}$  and at room temperature, and the curve derived by Dr. McAdam for a test at  $-188^\circ\text{C}$  with a sample of a different heat of Monel, are reproduced in fig. 12. The accurately determined flow-stress values for the test at  $-188^\circ\text{C}$  are plotted and designated by the subscript A in this figure. The symbols M, F, R and T represent the same quantities in this figure as in the author's paper. It is obvious that a flow-stress curve drawn



through the established points would not conform to the curve as derived by the author. A portion of the established curve between the points representing the drop of beam at yielding and the maximum load,  $M_A$ , falls considerably below the derived curve. The portion of the established curve  $F_A$  between the points representing maximum load and fracture would diverge from the derived curve and rise considerably above it at the beginning of fracture,  $T_A$ . The percent change in coordinates from  $R_A$  to  $T_A$  for the specimen tested at  $-188^\circ\text{C}$  is about one fifth that observed in the test with the same heat of Monel at room temperature and does not conform to the assumption made by the author in deriving his flow-stress curves at low temperatures, namely, that the percent decrease in coordinates from  $R$  to  $T$  should be the same for Monel tested at low temperatures as for Monel at room temperature. The flow-stress curve obtained with a specimen of the same heat of Monel tested in tension at  $-196^\circ\text{C}$  was almost identical with the curve obtained in the test at  $-188^\circ\text{C}$ ; it was slightly above the latter curve. However, the percent decrease in coordinates from  $R_A$  to  $T_A$  was approximately one half that obtained in the test at  $-188^\circ\text{C}$ . It is evident that the assumption used by the author to derive the points  $T$ , representing the beginning of fracture, for the low temperature tests is not valid.

The author's method of constructing the portions of the flow-stress curve representing the extension from yield to maximum load (fig. 1) may be questionable as indicated by the large variation existing between the established and the author's derived curve for a test at  $-188^\circ\text{C}$  as shown in fig. 12.

No mention is made by the author that the test data used by him for deriving the flow-stress curves for Monel at  $-188^\circ$  and at room temperature were obtained from annealed and cold-drawn specimens prepared from different heats. Some variation existed in the tensile properties at room temperature of the two heats as illustrated by the results obtained on annealed specimens as follows:

Property (Room Temperature)	Heat 1*	Heat 2†
Yield, 1000 psi	38.	35.
Ultimate, 1000 psi	88.	86.
Fracture, 1000 psi	211.	205.
$A_o/A$	4.0	3.58

\* Material used for testing at  $-188^\circ$  and  $-128^\circ\text{C}$ .  
† Material used for testing at room temperature.

There apparently are some errors in the reploting of the data for oxygen-free copper (fig. 3) from previous publications. The ductility value ( $A_o/A$ ) for the annealed copper tested at  $-188^\circ\text{C}$  is plotted as 5.9, whereas the determined value, as given in a previous publication,<sup>11</sup> was approximately 4.2. The fracture stress value for the cold-drawn copper specimen tested at  $-188^\circ\text{C}$  is plotted as approximately 122,000 psi, whereas the determined value, as given in a previous publication,<sup>11</sup> was approximately 145,000 psi. These corrections would alter considerably the positions and slopes of the corresponding flow-stress curves at this temperature. The tension tests at  $-128^\circ\text{C}$  with specimens of annealed and cold-drawn copper were not continued to complete fracture and no determinations were made of the fracture stress or ductility at fracture. Perhaps the author has used some extrapolated values. The determinations of the stress and ductility at the beginning of fracture of these copper specimens (except the specimens tested at room temperature) were not based on simultaneous load and diameter measurements during the tension test and should be considered only as approximate values. Simultaneous load and diameter measurements during the entire tension test are essential for an accurate determination of the flow-stress curve.

The author derives his  $F_o$  curves (flow under unidirectional tension) at low temperatures from the

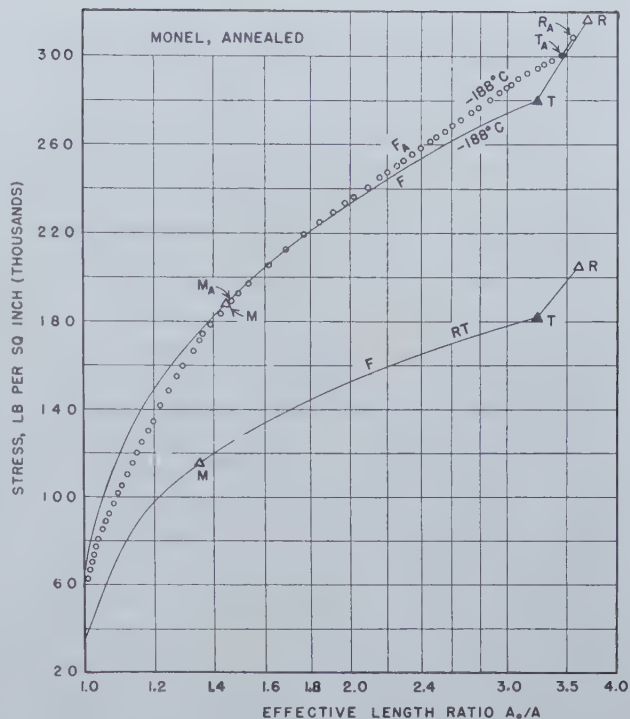


Fig. 12—Flow-stress curves.

corresponding  $F$  curves and the assumption that the triaxial stresses involved during the deformation from initial necking to fracture are the same as in the tests at room temperature; the  $F_o$  curves are constructed with the same percent deviation from the corresponding  $F$  curve as at room temperature. This assumption implies that the contour of the necked portion of the specimens during the deformation at different temperatures is similar. An examination of some specimens, tested at room and at low temperatures, in which the strains,  $A_o/A$ , from maximum load to fracture were the same, indicated that this assumption may not be valid. Although the minimum diameters of the necked areas were approximately equal, the necking generally extended over a greater length in the specimens tested at low temperatures than at room temperature. Thus the triaxial stresses involved would be different and the percent deviation of the  $F_o$  curves from the  $F$  curves at low temperatures probably should be less than that for the tests at room temperature.

As the "secondary," the "tertiary," and other derived curves developed by the author in the remaining figures of his paper are based on the flow-stress curves,  $F$ , and the derived  $F_o$  curves, in figs. 1, 2, and 3 and on additional assumptions, the validity of quantitative comparison of this series of derived curves is questionable.

G. W. GEIL, National Bureau of Standards, Washington, D. C.

D. J. McADAM, JR.—Mr. Geil's discussion exhibits a lack of perspective. An instance of this is his emphasis of the fact that the diagrams for Monel were from two different heats. In support of his idea that the heats differed significantly, he presents a table of tensile properties obtained with a specimen from each heat. The ultimate stresses of these specimens differed by 2.3 pct, the fracture stresses differed by 2.4 pct, the values for reduction of area evidently were 75 and 72 pct, and the difference in yield stress was unimportant. No better agreement in tensile properties would be expected if the tests had been made on two separately annealed specimens from the same bar, and greater differences might have been obtained with specimens from different bars of the same heat. The important property is the ultimate stress.

The heat designated No. 1 in the table is the one



used in obtaining the results in reference 11 of the paper. In that investigation and in others, Dr. Mebs and I had occasion to anneal many sets of specimens from numerous cold-drawn bars of Monel, all from the same heat. We found that the ultimate stresses of specimens from different annealing sets sometimes differed by several percent, especially when the specimens were from different bars. The range of values thus obtained was about twice as great as the difference in ultimate stresses shown in Mr. Geil's table. Evidence for this can be found by comparing figs. 3, 4 and 19 of reference 11.

Another instance of lack of perspective is Mr. Geil's use of his fig. 12. His discussion tends to give the impression that the two curves for  $-188^{\circ}\text{C}$  differ materially throughout the strain range beyond point M. However, the curves coincide throughout the important part of this range, and the extreme difference between corresponding flow stresses is about 6 pct. Not much better agreement would be expected if transverse measurements had been made during each test.

Between yield and maximum load the two curves differ greatly in form. Comparison with fig. 5 of the paper, however, shows that this difference would have no important effect on constant state curve A, would have no effect on curves B and C, and thus would have no appreciable effect on the graphically established points used in constructing the tertiary flow-stress curves. Moreover, the abnormal form of Mr. Geil's curve suggests that additional evidence is needed to determine whether the curve typifies the flow of Monel at  $-188^{\circ}\text{C}$ . Whereas the curve derived from the paper is similar in form to the curve established by numerous transverse measurements at room temperature, the curve presented by Mr. Geil cuts across in a nearly straight line between flow stresses 80,000 and 140,000, changes to another nearly straight line, and again bends abruptly near point  $M_A$ . No such form of curve has been obtained with Monel, copper or steels at room temperature.<sup>16, 17</sup> Moreover, Mr. Geil's curve differs greatly in form from the accurately determined curves obtained by Dorn, Goldberg and Tietz.<sup>2</sup> The curves obtained by these authors at low temperatures with aluminum, copper, brass, and magnesium are similar to those obtained at room temperature. The curve presented by Mr. Geil, therefore, evidently is not a typical flow-stress curve for  $-188^{\circ}\text{C}$ . The evidence thus tends to confirm the general usefulness of the procedure used in the paper.

Much emphasis is given by Mr. Geil to alleged errors in the plotting of values for the fracture stress and ductility of copper in fig. 3. Since the main purpose of the paper could be achieved as well without curves F and the points representing fracture, and since the construction of the diagram for Monel (fig. 2) is described in detail, it was considered necessary to use much less space in describing fig. 3 for copper. The true fracture stress for annealed oxygen-free copper cannot be determined even approximately by means of a conventional tension test. Consequently, in the investigation described in reference 11, Dr. Mebs and I used a much more tedious method in determining approximately the stress at the beginning of fracture. The tension tests were interrupted at frequent intervals, and transverse measurements were made. In the tests at low temperatures, this procedure involved the removal of the specimen before measurement and continuation of the test after the specimen had been cooled again to the low temperature.

By this procedure, the determination of the strain at the beginning of fracture is generally less accurate than the determination of the stress. Reconsideration of the evidence for the ductility of annealed copper at  $-188^{\circ}\text{C}$  led to the conclusion that the value of 4.2 indicated in reference 11 is too small, and that the value should be about 5.9 as indicated in fig. 3 of the paper. As would be expected, this value is greater

than the value obtained at room temperature. Since time was not available for the use of this slow procedure in the tests at  $-128^{\circ}\text{C}$ , the specimens were not extended to fracture. The fracture stresses for these specimens in fig. 3, therefore, have been determined by linear interpolation. As illustrated in figs. 19 and 20 of reference 11, the strength indexes for Monel and copper vary linearly with temperature on the scale used. The fracture stresses thus determined probably are as accurate as those determined directly at  $-188^{\circ}\text{C}$ . Because the fracture stress of the cold-worked copper at  $-188^{\circ}\text{C}$  was determined by a quick test in the conventional way, a correction was applied to give an approximate value for the stress at the beginning of fracture; the method of correction is the same that has been used for Monel (fig. 2). The flow-stress curves for the cold-worked copper in fig. 3 are merely qualitative representations added to complete the picture. They are not used in the derivation of other curves.

Mr. Geil apparently thinks that the object of the paper has not been attained unless the  $F_0$  curves for low temperatures have been extended with great accuracy far beyond the points representing the maximum load. The object of the paper, however, would have been attained if the  $F_0$  curves and the tertiary curves for Monel had been merely extended through constant-state curve C (figs. 4 and 5), and if the corresponding curves for copper had been merely extended through curve A (figs. 5 and 6). Although no allowance has been made for the well-known fact that the contour of the necked part of a specimen varies with the temperature, any resultant error in the divergence of the  $F_0$  curves would have practically no effect on the curves within the important strain range. In view of the fact that the error would be much less in the curves for  $-128^{\circ}\text{C}$  and  $-78^{\circ}\text{C}$ , than in the curves for  $-188^{\circ}\text{C}$ , a glance at figs. 5 and 6 will show that the only constant-state curve that might be affected appreciably is curve B for copper. In deriving fig. 8 some use has been made of the extended curves in the region beyond the constant-state curves of figs. 4 to 7. However, as illustrated in the left-hand diagram of fig. 8, the results were essentially the same as if attention had been confined to curves derived from the accurately established regions of figs. 4 to 7.

Curves  $F_0$  can be established with sufficient accuracy without the use of curves F. As shown in the paper, the ordinate ratios for curves  $F_0$  increase only slightly with extension beyond the points representing the maximum load. This relationship is in accord with evidence, which would require too much space for presentation here. Although the ordinate ratios increase continuously with plastic strain, nearly all the increase occurs between yield and maximum load.

The last sentence of Mr. Geil's discussion contains the amazing assertion that the secondary flow-stress curves (S) are based on curves F and the derived  $F_0$  curves. The paper is founded on the comparison of independently developed primary and secondary flow-stress curves. As previously shown, the tertiary curves are based on the accurately established regions of the diagrams. The final clause of Mr. Geil's discussion questions the "validity" of something that is not in the paper. No quantitative comparison of derived curves has been made. Moreover, no numerical value is mentioned in any of the conclusions at the end of the paper. However, if the word "quantitative" refers to the accuracy that might be expected in mechanical testing, quantitative comparison of the derived curves would be valid except possibly in the regions beyond the constant-state curves.

The following comment has no connection with Mr. Geil's discussion. Curves E in fig. 11 are based on the assumption that the variation of latent energy with plastic strain is in accordance with the diagrams presented by Taylor and Quinney.<sup>21</sup> In a recent study of the evidence, however, I have reached the conclusion



that the influence of plastic strain on latent energy is not in accord with the views of Taylor and Quinney. Curves *E* in fig. 11, therefore, are probably too steep. Moreover, I would now prefix to conclusion 10 of the paper the words, "For constant intrinsic strength."

## A Method of Examination of Sections of Fine Metal Powder Particles with the Electron Microscope

by L. Delisle

DISCUSSION, J. D. Shaw presiding

A. H. GEISLER—The magnification in this paper can be appreciated by the metallurgist only when the grain sizes are expressed in familiar terms. In fig. 3a, for example, the grain diameter is about 0.00001 in. which corresponds to the prodigious figure of 64,000,000,000 grains per cu mm. Where can one obtain a supply of the mounting plastic, aerotex M-3? What specific techniques were used to strip formvar or parlodion replicas from the surface or shadow cast for the various illustrations in the paper? Were the three basic types of structures in carbonyl iron powder associated with different conditions of formation?

L. DELISLE (author's reply)—I thank Dr. Geisler for his realistic illustration of the magnifications reported in this work. Aerotex M-3 is supplied by American Cyanamid Co., Textile Resin Department, Bound Brook, N. J.

Regarding stripping, the replica solution was poured over the surface of the specimens which were drained and allowed to dry. The replicas were then stripped with scotch tape on which the supporting screens had been placed. Before stripping, breathing on the specimen surface, covered with the dried replica film, helps in the removal of the replica. That method is one of the standard procedures used for plastic film preparation. References are given at the end of the paper.

Manganese, as mentioned in the paper, was the shadow casting metal.

The structures of carbonyl iron shown in the paper, as explained, were observed in the minute amount of powder used for one mount; that amount was taken from one sample of powder. For lack of information on the sample, the differences cannot be explained. The micrographs are simply intended to show the type of structure differences that can be brought out clearly by the electron microscope and would probably be missed in the light microscope.

A. H. GEISLER, *Research Laboratory, General Electric Co., Schenectady, N. Y.*; L. S. BUSCH, *P. R. Mallory Co., Indianapolis, Ind.*; R. STEINITZ, *American Electro Metal Corp., Yonkers, N. Y.*

L. S. BUSCH—Was there any correlation between surface characteristics and reduction practice? Was there any effect on the fabrication characteristics of the powder?

L. DELISLE—The paper was intended only to describe a method of preparation of metal powders for examination with the electron microscope. No correlation was therefore established between the structures and surface characteristics observed and the conditions of fabrication; it is hoped, however, that it was shown that such a correlation could be studied with the electron microscope when the details involved can no longer be resolved with the light microscope.

R. STEINITZ—Have you ever tried to make an electron micrograph of finer iron powder, about 1/10 micron in size, or do you think it possible?

L. DELISLE—It is probably possible to obtain electron micrographs of sections of iron particles, about 1/10 micron in diameter. The micrographs would show the size and shape of the section; they may not show structural details clearly. It is quite possible that modification of the techniques now in use would also permit

observation of such structural details within the particles. Outlines of the particles, dispersed in a supporting film, could no doubt be obtained easily.

## Determination of Boundary Stresses during the Compression of Cylindrical Powder Compacts

by M. E. Shank and John Wulff

DISCUSSION, J. D. Shaw presiding

P. DUWEZ and L. ZWELL—The authors have presented very interesting results on the side pressure distribution in a die. The reason for the difference between these results and those we published in their ref. 5 is possibly the fact that the motion of the piston we used in our measurements introduced some perturbing effect. According to our measurements, the radial pressure on the side of the die decreases from the piston to the center of the compact (supposing that both pistons are moving). This situation seems to be quite logical, since, as the length of the compact is increased (or more exactly, as the ratio of length to diameter is increased), the side pressure in the center must eventually become zero. It is indeed well known that for a long enough compact the powder in the center will not even be compacted; hence no side pressure could possibly exist. According to the authors' findings (which were limited to a length to diameter ratio of approximately 0.45) pressure in the center of the compact is greater than near the pistons. This type of side pressure distribution cannot logically persist if the length to diameter ratio increases. We wonder if the authors have any comments to offer on this subject.

P. DUWEZ, *Department of Mechanical Engineering, California Institute of Technology, Pasadena, Calif.*; L. ZWELL, *California Institute of Technology, Pasadena, Calif.*; F. V. LENEL, *Rensselaer Polytechnic Institute, Troy, N. Y.*; C. BIER, *Radio Cores, Inc., Oak Lawn, Ill.*; J. D. SHAW, *S. K. C. Research Associates, Paterson, N. J.*; J. F. KUZMICK, *Ekstrand and Tholand, New York, N. Y.*

M. E. SHANK (authors' reply)—Messrs. Duwez and Zwell's comment on an ever-increasing length of die causing the radial pressure at the center eventually to be zero is a very logical one. I believe there are two opposite tendencies operating here. In the case of very short compacts, since the densification of the center is not as great as it is near the plungers, the radial pressure in the center will be larger than the radial pressure at the more densified (almost solid) part toward the ends. This tendency will persist until the die is increased to a certain length and then the phenomena that Dr. Duwez mentioned will take over. The center of a long compact will be so far from the place where pressure is applied that the pressure in the center will be zero. Thus, for constant compacting pressure, a curve of radial pressure at the center would first rise, with increasing compact length, and then fall. We worked on very short compacts because the mathematical analysis got so very complicated for long compacts that we could not analyze some of the data we had.

F. V. LENEL—Will this method permit quantitative measurements of the influence of various lubricants upon die friction or will the effects that are measured by this method be so small that actual differences in die friction due to different lubricants cannot be measured quantitatively?

M. E. SHANK—I will agree with Dr. Lenel in that the precise quantitative measurements of the value of various lubricants cannot be made. We can from this method, however, qualitatively determine which of several lubricants might be better. We can rate them, say, one, two, three. We found stearic acid was better



than the others, but I cannot say numerically how much better.

C. BIER—There are two points that I would like to make about this paper. One is that in regard to the die lubricant I believe that the analysis similar to that which just has been reported on in this paper with the die lubricant mixed in with the powder rather than put on as a slurry on the die wall would be very interesting. It might, for example, bring out some of the answers to the questions that come up when we look at the results indicated by the strain gauges.

Another point that I would like to make is that in regard to Dr. Duwez' comments about what happens when we press a very long compact or briquette, one that has a great length in relation to its diameter, the straight line relationship shown between radial strain and material being used, might be somewhat less startling if we consider Dr. Duwez' comments. For example, we wonder why is there a straight line relationship with all the various powders on that straight line? It does not seem logical that such large variations in metal powders would all fall on the same straight line of a relationship between radial strain and briquetting pressure. If we remember that these metal powders have large variations in apparent density, we have the picture Dr. Duwez was making, the effect of a long, tall cylinder as compared to a short one. The answer to why we have the straight line is still not exactly clear because when we have metal powders which have large variations in apparent density we would expect the relationship that Dr. Duwez brings out, that is, a difference between a long cylinder and a short cylinder.

It is not clear to me why we have all these points for different metal powders falling in a straight line in a relation between briquetting pressure and radial stress.

M. E. SHANK—In regard to the placement of lubricants in the powder rather than along the die wall, this was considered in the paper of Kamm, Steinberg, and Wulff, in which they dissolved stearic acid in a liquid medium in vacuum, placed the powder in the resulting solution, evaporated the liquid and therefore left each particle coated with a layer of stearic acid. They did this for several compacts and found in all cases that lubrication of the particles in the compact had a very, very small effect compared to the efficiency of lubricant placed on the die wall.

With reference to the second question, this method is dependent for its measurement on the strain of the die. The strain on the die is going to be proportional to stress in the die. In other words, in this method we are not interested in the displacement of the powder itself; we are only interested in what happens as this powder pushes against the die wall and causes it to be displaced. Now it happens that regardless of powder particle size or distribution, the constraining body, which is the die, is distended a certain amount as the pressure is applied to the plungers, and consequently, the materials all fall in the same line. Lead, for instance, might flow more and the particles might deform more than a harder powder like iron, but nevertheless, the particles will tend to move outward against the constraint within the die and push against it.

J. D. SHAW—Has any work been done on the effect of highly polished surfaces and what differences such materials have on the test results? And also, what effect would such die materials as cemented carbide have?

M. E. SHANK—We wish to extend this work further. The die that we used has a very highly polished surface, as a matter of fact, a diamond lapped surface. From the work here, I would state the opinion that a rough surface would not change the values of radial pressure any but would certainly greatly increase the shear stresses on the die. I believe that this investigation should be pursued and we are going to pursue it, investigating the effect of surfaces such as tungsten

carbide and also the effect of wall smoothness or roughness on the pressing operation.

J. F. KUZMICK—I have been thinking a little more about this startling revelation today, that the type of powder does not have too much effect on the radial strain vs. the pressure applied, and I wonder whether we might explain that in a rather simple mechanical way. We know how we compress powder. We need very little pressure to consolidate the volume of powder to a considerable degree and it is only at the very end of the pressing stroke that we begin to get a compact that holds together.

In other words, if the compression ratio is 3 to 1, we might compress  $2\frac{3}{4}$  to 1, and if we ejected the powder from the die we would still have powder. Then if we increase that compression to say  $2\frac{3}{4}$  to 1, we have a compact that holds together, and finally, when we go to 3, only then do we have a dense compact. Therefore it seems to me, whether we use fine powder or coarse powder or whether it is copper or iron, the particles in effect are losing their identity as we approach the point where they cohere to form a compact which will hold together, and we are reaching a state where we are dealing with a mass of metal rather than powder.

We could look upon it as increasing the size of our die punch as we compress powder in the die. The portion nearest the moving punch, as pointed out, will get the greatest effect of that pressure, and therefore, we will get high densification of a layer of powder right next to the moving punch, so we might say that the punch has been increased in length by, say, a few thousandths of an inch. Then, as it comes down a little more, some of that pressure is lost due to friction between the first section of the compact and the die wall. Nevertheless, we will apply pressure to the next layer. In the meantime, our bottom plunger is doing the same thing from the opposite direction, and finally, when we get close to the end of our stroke we have in effect two longer punches with a very thin layer of powder in between.

In other words, if we began with an extremely thin layer of powder, whether it be copper or iron, or fine or coarse, I think we would find we would get just about the same radial pressure as the result of pressure applied to the die punch. And even in thicker layers of powder we approach that condition if we look at it as having rather solid metal next to it and free powder in the middle, and finally, in very long pieces we end up with a much longer punch, but most of our pressure has been lost due to friction, so we have uncompacted powder in the center and zero radial pressure.

M. E. SHANK—I think that is quite true, and that question can have further light shed on it if we press such things in the die as tungsten, which will not be plastically deformed to any extent, and lead, which will be greatly deformed and bonded.

## A Dilatometric Study of the Sintering of Metal Powder Compacts

by P. Duwez and H. Martens

DISCUSSION, R. P. Koehring presiding

D. D. HOWAT, J. P. CRANSTON, and R. L. CRAIK—We have read this paper with interest as we also have made quite an extensive investigation of the sintering of copper-zinc compacts and, to a smaller extent, of the sintering of the two pure metals.

We have not only used volume changes and X-ray diffraction methods to study the sintering process, but also changes in electrical resistivity and in heat absorption to obtain additional data, the latter investigations all having been carried out in vacuum.

At first, in all cases, resistivity increases with temperature as in a solid metal. This is followed by a rapid decrease in resistivity, heating being continued



until there is a linear relationship between resistivity and temperature.

Tests on pure copper compacts (compressed at 20, 50, and 80 tsi) showed a decrease in resistivity beginning at 80° to 100°C, a typical example of such a curve is shown in fig. 13. This, we believe, indicates the onset of sintering, although no volume change is recorded in the curves shown by the authors until a temperature of 800°F (425°C).

This may be explained by the assumption that copper particles, produced by atomization and subsequently compacted under high pressures, have a surface film of "disordered atoms." The first step in the sintering process may be a bridging effect between the disordered surface films of adjacent particles, thereby increasing the area of contact and decreasing the resistivity. Such a reaction may occur with no perceptible shrinkage and this suggestion may help to explain the gap of over 300°C between the temperature indicating the first change in resistivity and that at which shrinkage becomes perceptible according to the results of Duwez and Martens. We found no appreciable shrinkage in pure copper compacts up to a temperature of 650°C.

In general our volume change results agree very

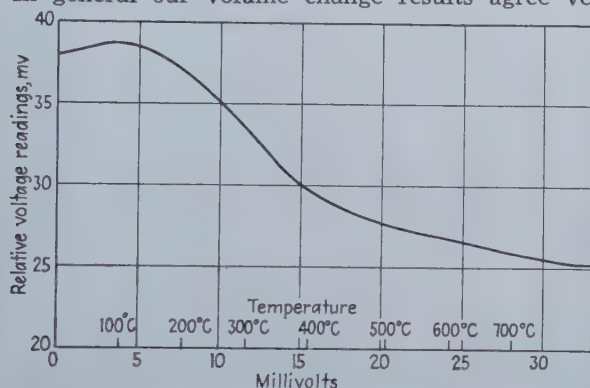


Fig. 13—Voltage curve. Pure copper compact of fine powder pressed at 50 tsi. Heated in vacuo.

closely with those of Duwez and Martens for the copper-zinc compacts, an example of our volume change curves being shown in fig. 14. Fig. 14 also shows the changes in resistivity in 60-40 copper-zinc compacts, made up in one case from a coarse copper powder and in the other from a fine copper powder. It is obvious that the major changes in volume and resistivity occur at the same temperatures in the copper-zinc compacts.

Finally, fig. 15 shows the differential thermal curve obtained from a powder compact using solid copper as a standard. Here again it is evident that the changes in heat absorption and in electrical resistivity and volume occur at the same temperature.

We agree with the tentative explanation offered by the authors that the zinc particles are absorbed by the copper particles which grow in size leaving cavities in spaces formerly occupied by the zinc. We suggest that this explanation may be amplified by assuming that the zinc is transferred to the copper through the vapor phase. The zinc, depositing on the copper, forms a film of alloy with a much lower zinc vapor pressure, so enabling further condensation of zinc to occur. Smigelskas and Kirkendall<sup>10</sup> have shown that the rate of diffusion of zinc into a copper-rich alloy is much more rapid than the diffusion of copper into an alloy with lower copper content, so that the zinc concentration in the surface film around the copper particles may remain at a level which gives a much lower zinc vapor pressure than that of free zinc. By extrapolating Hargreaves<sup>11</sup> data for the values of  $\log p_{Zn}$  against the reciprocal of temperature it is quite evident that a wide gap exists between the vapor pressure of zinc and that of the brasses at the temperatures in question.

An advantage of postulating the transfer of zinc to copper through the vapor phase is that the total sur-

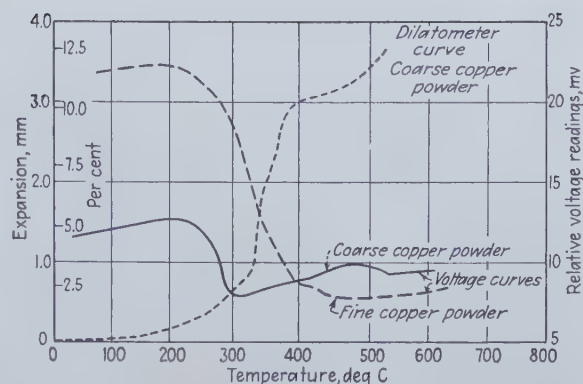


Fig. 14—Dilatometer and voltage curves. Copper-zinc compacts pressed at 50 tsi. Heated in vacuo.

face area of the copper particles may be taken as the diffusion interface in place of the much more restricted area involved if solid diffusion alone is postulated across the point contacts which may be assumed to exist between the constituent particles. The rapid disappearance of the free zinc and the formation of copper-zinc alloys at low temperatures is a most noticeable feature of this investigation and we suggest that the transfer of zinc through the vapor phase offers at least a partial explanation of this fact. Owen and Pickup<sup>12</sup> have shown that formation of the  $\beta$  phase, CuZn, (always the first product to appear) occurs within a few minutes when copper and zinc particles are merely shaken together and heated inside an evacuated sealed container. It is difficult to visualize such rapid transfer occurring purely by solid-solid contact.

Our results show that the volume changes increase progressively with zinc additions at least up to 60 pct zinc, the limit of our investigations. As this composition range includes the formation of  $\alpha$  and  $\beta$  solid solutions and of the  $\gamma$  phase, we feel that the suggestion put forward in the paper, that these large volume changes in sintering only occur in the case of simple solid solution formation, is inadequate to cover all the data.

As indicated, changes in volume, in resistivity, and in heat absorption may all be employed to indicate the onset and progress of sintering. In the case of the copper-zinc compacts the results obtained by all three methods are in close agreement. This is not shown in the case of pure copper compacts where changes in resistivity indicate the onset of sintering at temperatures far below those given by the volume and heat absorption changes.

We hope to publish a detailed account of our investigations in the near future.

P. DUWEZ and H. MARTENS (authors' reply)—We wish to thank Messrs. Howat, Cranston, and Craik for their interesting discussion. We believe that the transport of zinc through the vapor phase suggested by the discussers is a very probable mechanism. However,

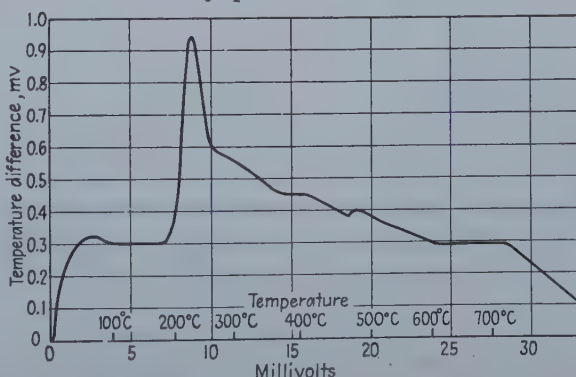


Fig. 15—Differential thermocouple curve. 60/40 copper-zinc compact (fine copper powder) pressed at 50 tsi. Heated in vacuo.



transfer of metal through the vapor phase is not an essential factor in promoting the growth of a compact. In the case of a copper-tin alloy, for example, steps in the thermal expansion curves are observed during sintering, although no tin could possibly be transferred through a vapor phase. This question has been discussed more completely in a paper presented at the International Congress of Powder Metallurgy in Graz, Austria, in 1948.<sup>18</sup>

The discussers seem to have slightly misinterpreted our conclusion relative to the case of metals forming solid solutions. As we explained in the paper, the fact that two metals form a complete series of solid solutions may prevent swelling of the compact. We never suggested the opposite point of view the reviewers infer by saying "large volume changes in sintering only occur in the case of simple solid solution formation."

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H. H. HAUSNER—In what atmosphere were the experiments made, and were big differences found in the results of the studies using various atmospheres for sintering?

P. DUWEZ (authors' reply)—All these experiments I just mentioned were made in hydrogen and also in helium. In both cases the shape of the thermal expansion curve was the same.

C. BIER—Are any data available from this dilatometric study for temperatures over 1400°F?

Dr. Duwez' point about the distortion of brass briquettes in commercial sintering being a function of the rate of heating is very well taken. Distortion may be overcome by packing the briquettes in bone black which results in a lower and more uniform rate of heating.

P. DUWEZ—The measurements were carried up to 1400°F only. At higher temperatures, shrinkage will probably proceed at a faster rate.

R. P. KOEHRING—Dr. Bier, do you think that in the example you referred to, the distortion could be attributed to the loss of zinc by evaporation and/or to the possible influence of the sintering atmosphere?

C. BIER—Mr. Koehring's remark about atmosphere is well taken since, when brass powders were initially being studied, there was considerable interest in the use of bone black as a helping agent for atmosphere. The experiment described was done with spent bone black present more as a packing agent than as a means of forming an atmosphere.

#### References

<sup>10</sup> Smigelskas and Kirkendall: *Trans. AIME* (1947) 171, 130; *Met. Tech.* (Oct. 1946) TP 2071.

<sup>11</sup> R. Hargreaves: *Jnl. Inst. Metals* (1939) 64, No. 1, p. 115.

<sup>12</sup> Owen and Pickup: *Proc. Royal Society (London)* (1935) 149A, 282.

<sup>13</sup> *Powder Met. Bull.* (1949) 4 (Nos. 5 and 6) 144-156, 167-174.

## Electrical Resistivity Measurements on Iron-silicon Compacts Prepared by the Powder Metallurgy Procedure

by F. W. Glaser

DISCUSSION, R. P. Koehring presiding

R. STEINITZ—During the course of Mr. Glaser's investigation of iron-silicon materials, we pressed a compact, half of which consisted of pure iron and the

other half of ferrosilicon. This compact was sintered at a fairly high temperature. I do not know the exact temperature, but I am sure that it was above the gamma transformation point of iron. The ferrosilicon contained enough silicon to suppress the alpha-gamma transformation completely. After sintering, the ferrosilicon part of the compact was fairly dense, but the iron part was still very porous. This again shows an agreement with Mr. Duwez' findings, that shrinkage in the alpha range is very much faster than in the gamma range. The ferrosilicon remained alpha while the iron had changed to gamma at the high sintering temperature.

At the AIME San Francisco meeting, a paper was presented in which the degree of homogenization of alloys was followed by magnetic measurements. We believe that resistivity measurements are very much better to follow the alloying process, as the magnetic properties are influenced much more by porosity than the electrical resistivity.

R. P. KOEHRING—How nearly would two adjacent specimens agree in electrical resistivity? In other words, how accurately can you measure resistivity and distinguish one specimen from another?

F. W. GLASER (author's reply)—The accuracy of the electrical resistance measurements for this investigation was very high if the cross-sectional area of the sample under test could be determined accurately. Electrical resistivity measurements in many cases permitted prediction of silicon content of the sample by the use of fig. 7, showing the percent silicon vs. electrical resistivity relationship.

R. P. KOEHRING—Would you expect that this method could be used for determining the degree of sintering of other metal or alloy systems besides iron-silicon?

F. W. GLASER—Yes. Though Hausner<sup>1</sup> employed the electrical resistivity of sintered materials as indicator of the degree of sintering, and Seelig<sup>2</sup> used resistance measurements for green strength determinations of powder compacts, it seems to me that this method of testing has also very definite limitations. Alloying and diffusion processes might readily be followed by changes in electrical resistance. However, work hardening and oxide films having distinct influence on the electrical resistivity of metal powders and compacts, might in some cases hide the real meaning of this test. The electrical resistivity is also influenced by the porosity, especially in low-density compacts.

R. P. KOEHRING—In other words, you believe this is most applicable to high-density materials which you made to a high density by high pressing.

F. W. GLASER—In view of the fact that low densities were avoided by the use of the hot-pressing method, the electrical resistivity measurements meant an accurate and fast method for determining the progress of diffusion in these alloys.

J. Q. ADAMS—Were there any particular controls on the ammonia atmosphere? Was it dry or wet ammonia?

F. W. GLASER—All heat treating was carried out in dry atmospheres: either in hydrogen or cracked ammonia. Although the purity of the atmosphere was controlled to a high degree by the use of drying towers and palladium catalyst, all samples were placed into special boats under an additional getter, consisting either of iron-silicon, iron-aluminum, or silicon powders.

J. T. NORTON—I think there is no question but what this discontinuity in the curve relating the resistivity to composition for iron-silicon alloys is due to the ordering, which takes place in the general composition range of around 16 pct. The ordered condition has been recognized previously and apparently the ordering persists to very high temperature, perhaps even to the melting point, so it is reasonable to expect that samples which are either quenched or slowly cooled from a temperature close to the melting point should give the same results. One would expect



to find a lower resistivity in an ordered alloy than in disordered alloys which exist at compositions on either side.

J. D. SHAW—There were two different density measurements obtained on three different compacts which had been sintered at increasing temperatures. All the compacts had about the same resistivity. I wonder if there is an explanation as to why they had the same resistivity, yet there was a wide difference in the porosity or density between one of these and the other two.

R. STEINITZ, *American Electro Metal Corp., Yonkers, N. Y.*; R. P. KOEHRING, *Moraine Products Division, General Motors Corp., Dayton, Ohio*; J. Q. ADAMS, *General Electric Co., Schenectady, N. Y.*; J. T. NORTON, *Massachusetts Institute of Technology, Cambridge, Mass.*; J. D. SHAW, *S.K.C. Research Associates, Paterson, N. J.*

F. W. GLASER—The materials you refer to have been tabulated in table III, and contain 33.5 pct silicon. In the higher density ranges, the resistivity varies only very little with decrease of porosity.

R. P. KOEHRING—I have another question in regard to the lower density materials. Would it not be possible to compare resistivity measurements on materials of corresponding density? You said you could not use this method on low density materials, only on materials that are of maximum density. If you compared the resistivity measurements against completeness of sintering on materials of similar lower density, would you not still get a correlation?

F. W. GLASER—Yes. I believe you will be able to compare specimens for their completeness of sintering if their densities are alike, or nearly alike, even in lower density ranges.

#### References

<sup>1</sup>H. H. Hausner: Symposium on the Physics of Powder Metallurgy. Sponsored by the Sylvania Electric Products Co., Bayside, L. I. (Aug. 1949). To be published.

<sup>2</sup>R. P. Seelig: *Ibid.*

## The Yielding and Strain-aging of Carburized and Nitrided Single Crystals of Iron

by H. Schwartzbart and J. R. Low, Jr.

DISCUSSION, R. W. E. Leiter presiding

A. N. HOLDEN and J. H. HOLLomon—A detailed analysis of Schwartzbart and Low's data indicates that it has not yet been demonstrated that single crystals of iron exhibit a drop in load and constant lower yield stress upon initial yielding. The present paper brings into focus the confusion as to the nature of the initial yielding of steel and emphasizes the need for additional careful experimental research. It can now be concluded definitely, however, that even if single crystals of steel are subsequently shown to have an initial drop in load and lower yield-point elongation, this elongation will be found to be significantly smaller than that of fine-grained polycrystalline specimens.

In order to emphasize the contradictions in Schwartzbart and Low's research, a detailed analysis of their results follows.

Crystal No. 2, the data for which are in fig. 9, exhibited no trace of a yield point in either the carburized or decarburized condition.

If the "drop in load" in the flow curve of carburized crystal No. 3, fig. 11, is considered a yield point, the horizontal part of the initial flow curve of the decarburized crystal No. 3 is also a yield point. Furthermore, the two crystals labeled No. 3 and purportedly of the same orientation have a large difference in elastic moduli.

Of all the crystals tested, crystal No. 4, fig. 13, lends

the most support to the authors' contentions concerning the yield point.

The initial drop in load and yield-point elongation of the non-nitrided crystal No. 5 of fig. 15 is greater than for all other carburized or nitrided crystals except crystal 5 when nitrided.

Crystal No. 6, fig. 17, shows no definite drop in load in either the nitrided or non-nitrided condition.

Crystal No. 7, fig. 19, fails to show any yield point either nitrided or after wet hydrogen treatment. Again the moduli of two purportedly identically oriented specimens are vastly different.

It is apparent from figs. 10, 12, 14, 16, 18, and 20 that all the crystals that supposedly contain nothing to cause strain-aging—that is, no carbon or nitrogen—do strain-age. Therefore, they must not have been thoroughly decarburized.

In summary, crystals 2, 6, 7, exhibit no yield whether they contain carbon or nitrogen. Slight indications of a yield point were found for crystals 3, 4, and 5 in the carburized or nitrided conditions. However, yield points were also observed for crystals 3 and 5 in the "carbon and nitrogen-free" condition; in fact, 0.4 pct yield-point elongation was measured for crystal 5 after wet hydrogen treatment.

An alternative conclusion, equally tenable with that of the authors', is that all the crystals that did have initial yield points, exhibited them as a result of deformation followed by aging prior to testing. It is not unlikely that a repetitive procedure of straining slightly, observing the alignment, resetting grips, and restraining until alignment is accomplished, could deform the crystals enough to cause strain-aging.

The crux of the experimental problem, then, since it is now known that iron crystals will strain-age, is to prove beyond a doubt that the initial yield point occurs in a perfectly aligned, previously undeformed crystal and not as a consequence of strain-aging. Certainly experiments in which only half of the crystals show an initial yield point are not conclusive. Admittedly, it is also just as important in any experiments in which no yield point is observed to demonstrate that slight misalignment has not obscured a slight yield point. It is possible that in our (Holden and Hollomon<sup>11</sup>) experiments, lack of alignment could have obscured a small yield-point elongation.

It appears that it has now been demonstrated that iron single crystals strain-age, and that the yield point elongation of single crystals tested at room temperature is very small if not nonexistent.

A. N. HOLDEN and J. H. HOLLomon, *General Electric Co., Schenectady, N. Y.*; R. MADDIN, *Johns Hopkins University, Baltimore, Md.*; R. W. E. LEITER, *The Budd Co., Philadelphia, Pa.*

H. SCHWARTZBART (authors' reply)—First, the authors agree that the yield-point indications in the single crystals are very slight compared to the magnitude of the effect in the polycrystalline samples.

In regard to the inconsistency of behavior from crystal to crystal, the authors believe the explanation is that mentioned in the presentation of the paper. Apparently none of the crystals was completely decarburized and denitrided, as was hoped would be the case. The traces remaining were sufficient to make these specimens exhibit yield-point behavior.

In regard to the reasons for some of the carburized or nitrided crystals not showing yield-point behavior, I should like to point out that the effects are small and tend to be obscured by all of the experimental difficulties. The fact that a yield point was ever obtained should certainly be significant.

Holden and Hollomon suggest that the yield-point indications obtained in the initial tests were the result of strain-aging, the strain having taken place during alignment of the specimen in the machine. The authors cannot agree with this notion for the following reasons. Extreme caution was observed in order not to strain the specimen before inserting in the machine.



The strains during alignment were elastic. Even granting there was any plastic straining, it must have been extremely small; but even granting the amount was enough to cause strain-aging, it is very unlikely that the time at room temperature between aligning and testing was sufficient to cause strain-aging.

In connection with our work, I should like to describe some results obtained by Cottrell and Gibbons<sup>20</sup>

<sup>20</sup> A. H. Cottrell and D. F. Gibbons: Thermal Hardening of Cadmium Crystals. *Nature* (Sept. 25, 1948) 162, 488.

on cadmium single crystals which exhibit a drop in load similar to mild steel. I will not describe their experiments in detail, but the gist of it is that carbon crystals grown in nitrogen showed a drop in load in the annealed condition. The annealing was done with the specimen in place in the tensile machine. Crystals which were grown in argon, however, showed no drop in load. The nitrogen affected the yield-point behavior of the cadmium crystals the same way we believe it affected the iron crystals.

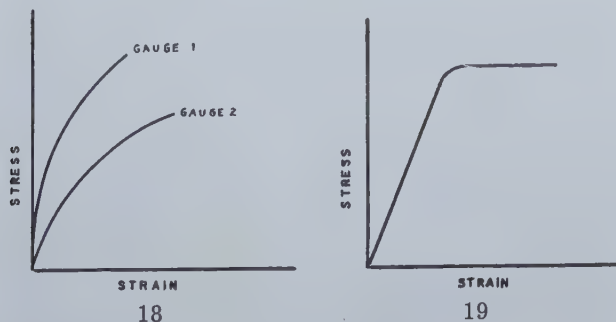


Fig. 18—Eccentrically loaded single crystal. Gauge 1 is 180° from gauge 2.

Fig. 19—Axially loaded single crystal with same orientation whose stress-strain curves are plotted in fig. 18.

R. MADDIN—I should like to report some related work that was done at Yale, about a year and a half ago, regarding yield point in brass crystals.

A long, brass, cylindrical single crystal was cut into two parts. On attempting to investigate the yield phenomenon, strain gauges were placed at four different positions, 90° apart.

In one of these crystals the stress-strain diagram was plotted using strain gauges, 180° apart. The two curves for this crystal are illustrated in fig. 18. On the second crystal, some degree of accuracy in axially of loading was assured and a very well-defined yield point is evident in fig. 19.

These figures clearly illustrate the necessity for exact axially since the introduction of any eccentricity will produce plasticity on one side of the crystal prior to plastic action on the other side.

J. H. HOLLOMON—I should like to point out the importance of this problem to the general problem of deformation, and to indicate some of the reasons for the interest in it. There are many theories of deformation, but there is only one that seems to explain most of the observed effects. This is the theory of deformation by the propagation of pre-existent dislocations. This theory has made only one prediction, however, and that is that single crystals of iron should exhibit yield points. If they do not, less credence would then be given to current dislocation theory. Even if yield points of small magnitude are found, the theory still has to explain the tremendous difference in the behavior of single crystal and the polycrystal. If the yield-point effect is not observed in single crystals of iron, if it is absent, as far as I can see, it means that the dislocation mechanism as proposed by Taylor, Orowan, Becker, Cottrell, etc. must be severely modified.

R. W. E. LEITER—I should like to ask the authors if they observed surface markings on the test piece dur-

ing the test. Heterogeneous flow is thought always to accompany the sharp yield point and therefore any data on the presence or absence of Lüders lines would be of value.

J. R. LOW, JR. (authors' reply)—In reply to Mr. Leiter's question it is obvious that this investigation is incomplete, and also Holden and Hollomon's, in certain respects. We did not examine all possibilities, such as structural changes and, further, as a result of the manner of testing, it was not possible to observe the surface during the deformation, so that we cannot say anything about whether or not a heterogeneous deformation accompanies the drop in load.

I would like to summarize the position at the moment. If you will recall, Holden and Hollomon found absolutely no indication of anything resembling what we call the yield point in their crystals. We have not always found this yield-point phenomena in ours. I think that it might be argued that there was a possibility of minute plastic strains in our crystals before they were tested. This is a pretty hard thing to rule out absolutely, if one is dealing with extremely small strains, so that there is some possibility that strain-aging may enter into the yield-point indications that we did observe. On the other hand, I think there is good reason to believe that Holden and Hollomon's crystals were not very well aligned. As Dr. Maddin has pointed out, this has a profound effect on the behavior at the beginning of flow.

## Size Effects in Quenching High-purity, Precipitation-hardenable Alloys

by W. L. Finlay

DISCUSSION, T. L. Fritzlen presiding

T. L. FRITZEN—With reference to Dr. Finlay's paper, I would like to state that we have found variations in hardness from the center to outside in heavy 14S-T6 and 25S-T6 sections produced commercially. The center of the heavy section was found to have lower hardness than the outer areas.

T. L. FRITZLEN, Reynolds Metals Co., Richmond, Va.

W. L. FINLAY (author's reply)—The work reported in the paper showed that high purity aluminum-copper and aluminum-zinc in sections thicker than 1/10 in. gave "anomalous" precipitation hardening whereas commercially pure 24S and 75S did not. If these results can be generalized, the hardening variations in commercially pure 14S and 25S reported by Dr. Fritzlen are not related to the effects reported in the paper. The indication of the latter is that the combination of high purity and specimen thickness greater than perhaps 1/10 in. may give greatly variable precipitation hardening behavior in aluminum-base, precipitation-hardenable alloys.

## Secondary Recrystallization in Copper

by M. L. Kronberg and F. H. Wilson

DISCUSSION, W. R. Hibbard, Jr. presiding

C. H. MATHEWSON—As the study of structural changes during plastic deformation, recrystallization, diffusion, and heat treatment, generally advances towards a clear interpretation of these complicated processes, this paper will be recognized as a milestone of progress in this all important field of theoretical metallography. In considering the origin of textures or other structural readjustments it is often necessary to contemplate rotations as well as translations of parts of the crystal, or blocks, relative to other parts. If a block of considerable size is rotated around a central axis, its outermost atoms obviously become widely separated from the atoms of the matrix and this intolerable condition of strain would have to be relieved by some appropriate slipping process. It has lately been demonstrated<sup>20</sup> that even the simplest straining mechanism of



a single crystal is accompanied by slip on more than one (the classically predicted) set of octahedral planes, doubtless to accommodate the rotations which must occur in order to maintain a proper axial condition as the shape of the specimen changes when its parts move against one another.

What the authors have done, apart from the factual data in this paper, is to demonstrate how a nucleus or domain within a crystal can change its orientation, or rotate around a crystallographic axis and grow without introducing the considerable strains just mentioned. It seems highly probable that this sort of a mechanism operates in recrystallization, perhaps in plastic deformation in conjunction with slip, and very likely in diffusion. Probably the essentials of this structural change are recorded in the literature of crystallography but this in no way detracts from the initiative of the authors in pointing out the fundamental application to metallurgy.

I shall discuss only this aspect of the paper and will call your attention first to the crystallographic nature of the process. Fig. 26 shows, at C, the northwest pole of the octahedral plane carrying the indexes of important planes in this zone. It is seen that directions of the form  $\langle 213 \rangle$  can be superposed by rotating either through a small angle, which is  $22^\circ$ , in one direction, or through a larger angle,  $38^\circ$ , in the other direction. This of course brings the lattices into coincidence along the line in question when one plane is rotated above or below the other. This condition is shown for a  $22^\circ$  counterclockwise rotation in the authors' fig. 13, with respect to the sites of all atoms when three planes, making a completed lattice, are rotated around an axis centered at one of the circled large black sites. It is important in considering this figure to realize just how the authors have designated all of the sites. The large black sites represent the central plane, the smaller black sites may represent the lower plane, and the smallest black sites the upper plane, all in their original positions. The large open sites represent the rotated positions of the atoms in the central plane, the smaller open sites, the rotated positions in the upper plane, and the smallest open sites, the new positions in the lower plane. Observe that the atoms of the lower plane have been given the rotated positions of the atoms in the upper plane and vice versa. And they have reached these positions by local rotations involving small displacements around the sites which would be found in coincidence if a bodily rotation of the planes (as described earlier) took place. This is the fundamental operation advanced by the authors, and it is important to examine it with respect to the nature of the twin fault which they regard as a possible activating cause of the process.

Referring again to fig. 26, assume simple extension of a crystal whose axis is located at P, bringing into operation as a primary slip system the plane whose pole is at D and the observed direction IV. We customarily say that the slip direction moves towards the axis which is the enforced direction of flow of the material, i.e., the active component of stress is resolved in the conventional slip direction and the force is acting along rows or strings of close-packed atoms lying in the direction IV. But it has been my view for many years, as stated by the authors on pp. 509-510, that the atoms cannot move over one another in the close-packed direction but must move in the valleys which are  $\langle 112 \rangle$  directions. Ideally, this may be viewed as two-stage slip, yielding an integrated displacement in the close-packed direction. However, the first movement produces a twin fault and if it persists or can be recognized through some characteristic after effect, as may be argued in the present case, there is ground for belief that in some stage of the slip process only this first stage of slip takes place (in many locations) owing to some interference, by cross-slip, or otherwise, with the second stage. While the normal stacking of planes in the face-centered cubic lattice exhibits the two  $\langle 112 \rangle$  directions, a and b, shown in

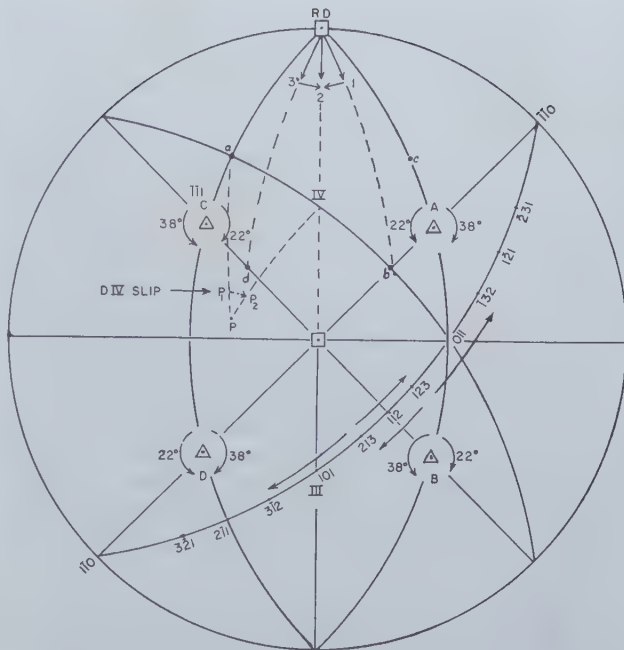


Fig. 26—Lattice rotations during  $\langle 112 \rangle$  slip.

fig. 26 to the left and right of close-packed direction IV, the first stage movement for extension must be in the direction a. This is the movement which would permit an upper block to shear over a lower block with a resulting obtuse angle between the two, as required for extension. The other movement could not take place as a first stage except in the reverse direction corresponding to contraction.

In order to direct the basic flow direction resulting from shearing movements between many planes in the a direction, towards the flow direction prescribed by the axis, the crystallite rotation, or the rotation in the affected part of the crystal must be along the great circle joining A and a, say to the point P<sub>1</sub>. However, the component of stress which forces the entire process of slip and orientation is in the close-packed direction IV requiring a rotation along the great circle joining P and IV and this stress condition requires that an axial position P<sub>1</sub>, corresponding to the rotation previously described, should move towards P<sub>2</sub>, i.e., a rotational strain in the crystallite around the pole of the slip plane D. Such a rotational strain at the slip site is opposed by the body of the crystal adjacent to the plastic disturbance. In an elastic process, strain would disappear on release of load, but in the plastic process at hand, almost certainly involving cross-slip and slip on conjugate planes, a condition of residual stress persists and it is believed that its relief would require rotations in opposition to one another in the vicinity of slip sites.

In order to visualize the changes which might be necessary to produce such a result, fig. 27 has been prepared. The stacking is shown below with numbered sites. Here, the sites in the lowest plane are numbered, 3, in the next above, 2, and in the uppermost plane, 1. In the upper part of the diagram, this stacking is shown through a group of eight planes at the left. The operation of producing a twin fault by slip at one site in the  $\langle 112 \rangle$  direction, 1 to 3 in the lower sketch, produces the alteration in stacking shown in the column to the right of the arrows. As 1 moves to 3, all of the planes above move with it and, for consistency with the authors' fig. 13, dots of three sizes are included along side the numbered sites to show the relative positions of the atoms in the various planes. This bodily movement of a group of planes over another group does not show the true positions of the planes or the elastic strain after shear, because in reality the upper group moves in one direction and the lower group in



the other direction, with the customary rotation and its associated strain, to preserve axiality. But it does grossly exhibit the altered stacking.

Now the upper bracketed group of four planes may be brought to the twinned stacking either by 38° clockwise rotations of all the atoms shown around a coincidence site, 3, or by the exact rotations used by the authors in fig. 13. These are 38° clockwise rotations of upper and lower planes around the three coincidence sites respectively. It is not feasible to examine the rotations of fig. 13 during discussion but the result is shown at the right in the present diagram. In numbering the site changes, primes are used against the numbers because all of the sites are moved into corresponding positions given by the gross reorientation of the crystal. That is, the crystal as a whole is rotated 22° counterclockwise, but this part is twinned by rotating the original atoms 38° clockwise into twin positions.

The lower bracketed group of four planes is now reoriented by rotations of all the atoms 22° counterclockwise in groups around coincidence sites, 3, which correspond to the site around which the gross reorientation of the crystal was effected. This part is thus

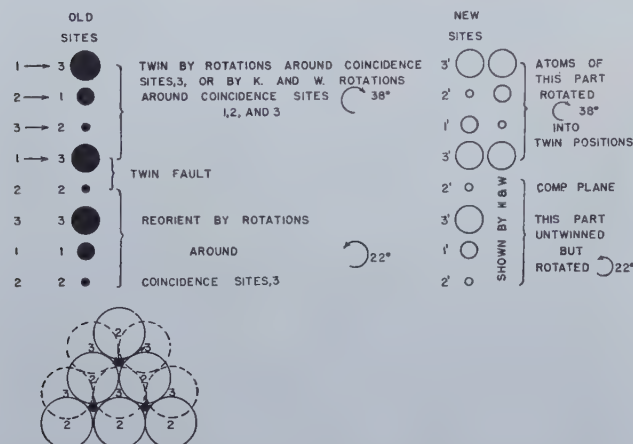


Fig. 27—Growth of a reoriented twinned crystal from a twin fault.

rotated 22° throughout and remains untwinned. The alternative operation of rotations around the three different coincidence sites cannot be used in this case. If these rotations are performed completely throughout the structure shown in the authors' fig. 13, atoms at the coincidence sites numbered 3 are of course left unchanged. But those at the other centers shown in fig. 13 (triangles and dots) have to move so as to change sites around the outermost circles which would be described about the coincidence sites, 3.

Not enough is known about the complete strain pattern in the deformed crystal to argue the competence of the alternative methods offered for the rotation into twin position, namely, use of a single set of coincidence sites as axes of rotation, or use of all three sets. As may be seen at the right of the diagram the structural change that occurs in the suggested process is a growth of reoriented twinned crystal on one side of the twin fault and a growth of reoriented untwinned crystal on the other side with a composition plane, numbered 2', joining the two parts. This is in accord with many observations of recrystallized structures.

Finally, it is of the greatest importance in evaluating the authors' results to consider the polarity of the rotations. One of their principal observations was the restriction of reoriented octahedral poles in the recrystallization of their rerolled "cubically aligned structure" to positions which would correspond to clockwise rotations of what seem to be basically 22° and counterclockwise rotations of 38°, respectively, around the northwest and southeast poles or counterclockwise rotations of 22° and clockwise rotations of 38°, respectively, around the northeast and southwest poles. This cannot have its origin in the fundamental

crystallography of the process because, as already pointed out, symmetry relationships permit no such restriction of polarity in the coincidences of  $\langle 321 \rangle$  directions by rotations around the octahedral poles.

It is suggested that this restriction is inherent in the slip process and depends upon the polarity of the rotation,  $P_1$  to  $P_2$  shown in fig. 26 when properly associated with the slip directions which are active in the given process. In the present case, the cubic texture has slip directions III and IV lying in the lateral planar boundaries of the strip as it lengthens in rolling. If these actually dominated in the direct rolling of the cubic texture, they would by their slip and rotation permit the strip to elongate in the rolling direction and contract along the strip-normal without spreading sideways, as must be required. Consider first the action of direction IV in the plane whose pole is located at D. For consistency with the stereographic charts shown by the authors, let the upper cube pole represent the rolling direction. The central pole then represents the strip-normal which must contract in the slip process. For elongation of the strip the axis in question (upper cube pole) must move towards the slip direction concerned, i.e., the direction which was at RD moves towards IV. But we are postulating slip in a  $\langle 112 \rangle$  direction,  $a$  or  $b$ , to the right or left of IV as we observe from RD. When octahedral planes move over another in  $\langle 112 \rangle$  directions of the face-centered cubic lattice there is a directional restriction.\*

\* I have found no simple way to demonstrate this in the stereographic projection. It is best to consider the atom sites in detail with a model and trace the appropriate movements for extension or contraction.

If a certain direction is prescribed, the atoms can move in this sense along a selected  $\langle 112 \rangle$  lattice line but would have to move in an opposite sense along an adjacent  $\langle 112 \rangle$  lattice line. In this case the  $\langle 112 \rangle$  slip and rotation producing elongation of the crystal correspond to movement of RD (the axis) towards,  $b$ , the  $\langle 112 \rangle$  line which lies farthest from the cubic axis. The movement of the axis is therefore in the direction of the arrow to some point 1. But the conventional  $\langle 110 \rangle$  slip and rotation are represented by the arrow in the direction IV to some point 2 and the rotation around the pole of the slip plane (D) which would direct the  $\langle 112 \rangle$  flow direction towards the normal  $\langle 110 \rangle$  flow direction determined by the fundamental action of stress along a close-packed lattice line, is indicated by the arrow from 1 to 2. This is viewed as the counterclockwise rotation observed by the authors as a 22° rotation around pole D.

Consider, similarly, the same direction IV in a plane whose pole is located at B. The corresponding  $\langle 112 \rangle$  lattice lines are at  $c$  and  $d$ . Observing at RD, the movement towards the righthand  $\langle 112 \rangle$  lattice line,  $d$ , i.e., the  $\langle 112 \rangle$  direction farthest from the axis, leads to some point 3; the conventional slip and rotation are as before and the corrective rotation around the pole of the slip plane B is clockwise as shown by the arrow from 3 to 2. This is considered to be the clockwise rotation observed by the authors as a 22° rotation around pole B.

Similar analyses of the action of direction III in the planes whose poles are located at C and A lead to a counterclockwise rotation around A and a clockwise rotation around C in correspondence with the authors' fig. 9.

This long discussion will be concluded with a few words about the significance of the reorientations produced on annealing the cubically aligned strip when activating nuclei are present. When part of the crystal is rotated about the normal to an octahedral plane 22° in one direction there is the crystallographic requirement that an adjacent part be rotated 38° about the same axis in the other direction in order to produce a stable twin complex. The rotations analyzed are the ones which I have associated with a presumed direction of elastic (or anelastic) strain at a hypothetical twin fault and a reactive (opposite) strain in the adja-



cent crystal. Nothing is known about the magnitude of these strains but they are used to activate the 22° and 38° rotations which remove the strain from the affected planes and produce a structurally homogeneous twin-complex whose adjustment to the surrounding material is of course characterized by strain at its boundaries. Further growth of the twin crystal in one direction or another parallel or normal to the composition plane would of course be activated by this boundary strain as in the general process of grain growth. It is believed that variable strain patterns exist in the neighborhood of twin faults due to various causes such as cross-slip or perhaps dislocations of one sort or another. These of course would cause variable growth effects but it is important to note that the polarity effects and the general crystallographic features of the observed recrystallization pattern are in harmony with the analysis given in this discussion.

C. S. SMITH—The authors have considered the points of lattice coincidence only on the basis of a two-dimensional plane interface. It might be advisable to consider these things three-dimensionally. It is possible that the authors' points of lattice coincidence correspond to positions at which, by an appropriately warped interface, the two lattices can be completely coherent and continuous with each other.

P. A. BECK—This paper is very interesting. Many of the experimental results in it are in excellent agreement with those observed independently and published practically simultaneously by two other groups of investigators, namely, by Beck and Hu<sup>21</sup> and by G. W. Rathenau.<sup>22</sup> The close agreement in the experimental results in these three investigations certainly emphasizes the reliability of the results. We can now accept with a considerable degree of assurance that in face-centered cubic metals the major part of the orientation change in coarsening corresponds to a rotation around a  $[111]$  axis—a fact first discovered by Bowles and Boas.<sup>23</sup> In the work of Bowles and Boas tough pitch copper and in that of Kronberg and Wilson OFHC copper was used; both materials were of commercial purity. Rathenau worked with a face-centered nickel-iron alloy of commercial purity. It is significant that the orientation relationship found by Beck and Hu is practically the same, even though the process in these experiments was a pure-bred instance of texture-dependent coarsening, with practically no dispersed second phase particles present, while in the investigations with commercial purity metals the inhibiting effect of the particles of dispersed phases could not have been negligible.

I wish to emphasize the excellent agreement of the orientation relationships found by the three groups of investigators mentioned since it is in notable contrast to the differences in certain of the interpretations. The main difference between Kronberg and Wilson on the one hand and Beck and Hu and Rathenau on the other hand, relates to the question whether these orientation relationships result from oriented nucleation or oriented growth. These questions will be discussed more fully in connection with the paper of Beck and Hu.

One of the interesting new observations found by Kronberg and Wilson is that, in addition to the  $[111]$  rotation, coarsening in commercial purity OFHC copper may lead also to grains with certain other orientations, similar to those found by Rathenau in Ni-Fe alloys.

Another interesting result, very satisfactorily shown by Kronberg and Wilson, relates to the shape of the coarse grains growing in copper. These grain boundary shapes indicate clearly that surface energy must be at least a contributing factor of growth in coarsening. I am inclined to agree with the authors that very likely it is the only driving force, although Rathenau takes the point of view that the driving energy is derived from the small residual strains remaining in the recrystallized grains. My belief that Kronberg and Wilson are correct in this respect is based on the observation that very often a considerable extent of gradual

grain growth takes place between recrystallization and coarsening. In such cases any residual strains that may have been retained during recrystallization must have been certainly eliminated during the grain growth process; subsequent coarsening must have had a driving force other than that postulated by Rathenau. This view is further supported by recent work of Guinier and Tennevin,<sup>24</sup> with Rathenau's samples. Even by using the best available X-ray diffraction methods, these investigators could not distinguish between the degree of crystalline perfection of the coarse grains and that of the fine-grained matrix in which they grew.

C. G. DUNN—The authors have presented a very interesting paper both with regard to new knowledge concerning recrystallization phenomena and to stimulating ideas on possible mechanisms of recrystallization. In contrast to other investigators they have found a somewhat different and more exact orientation relationship between the large secondary twin grains and the primary cube texture matrix for an active  $\langle 111 \rangle$  axis—the common  $\langle 111 \rangle$  axis of the twins, which also is a  $\langle 111 \rangle$  axis of the cube texture. The asymmetry found relative to rotations about  $\langle 111 \rangle$  axes, which reduces the final symmetry from four-fold to two-fold, is an interesting new feature.

In agreement with results obtained by Turkalo and Turnbull,<sup>25</sup> the authors find it necessary to add strain to a sharp, cube texture, fine-grained matrix to make it undergo secondary recrystallization. They also find that the resulting texture is essentially the same as that obtained for secondary recrystallization proceeding without added strain in a matrix, which occurs

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when the cube texture is not so strong. This circumstance adds credence to the idea that a nucleation process is involved in secondary recrystallization regardless of added strain.

The authors consider that twins have to be present before secondary recrystallization will occur without added strain and that when strain must be added, the strain must generate twin faults. According to this view a stable, strong, cube texture matrix is one free of twins or twin faults. However, if we assume a strain-free matrix in the usual sense as the authors do, it is difficult to envisage a nucleation process involving the action of a twin, say at a grain boundary position. The question arises "How large must a new grain or twin pair become before it can continue to grow using grain boundary energy alone as the driving force?" The answer, I think, is a grain certainly larger than that of other matrix grains. This idea was discussed briefly in a paper<sup>26</sup> given a year ago. The arguments involve the view that boundary energy for grains differing only a small amount in orientation is small compared with the energy normally encountered for grains differing appreciably in orientation (this view the authors also accept). Geometrically this picture means that an "off-orientation" grain surrounded by grains in the  $(100) [001]$  orientation would be nearly equivalent to an island grain in a single crystal and would tend to disappear unless already above a critical size. Since the critical size of a nucleus increases with decrease in energy per unit volume of a strained matrix, it appears obvious that the critical size of the off-orientation grain would be appreciably above that of the other grains. That a grain could start from submicroscopic size and grow large enough by statistical fluctuations to pass over the energy hill and complete the nuclea-



tion process as needed here seems very doubtful. Even with additional energy arising from a favorable change in lattice arrangement at the surface of the sheet, as the authors suggest, it does not seem likely that such a nucleation process could occur.

If we are to have a nucleation process then, it seems to me that some strain energy is required in regions of the crystal lattice. As pointed out by Bowles and Boas,<sup>23</sup> it is entirely possible that part of the matrix becomes strained during a primary recrystallization process. The present writer has observed<sup>27</sup> individual grains in silicon iron with appreciable strain resulting from primary recrystallization of deformed single crystals. Turkalo and Turnbull<sup>25</sup> noted an effect of type of annealing on stability of the strong, cube texture material, and this may mean an alteration of self-straining with the manner in which primary recrystallization occurs. Finally, one has to suppose a relation between self-straining and degree of texture formation to account for nucleation without the added strain for the weaker cube texture materials.

The question also arises "Can all the facts regarding secondary recrystallization be explained without a nucleation process—that is by exaggerated grain growth?" It seems doubtful to me that they can. Twinning during growth, for example, in a manner called repeated twinning, and this occurs quite often in copper, is not at all the same as growth of a twin pair. Nucleation during growth is required whenever several orders of twins occur or whenever more than one twin per grain forms. Such twinning occurs frequently during recrystallization in silicon iron when strain, of course, has been added, but apparently never occurs during exaggerated grain growth when strain has not been added. It may, however, be argued that the energy required to nucleate a twin in the body-centered cubic lattice is no doubt much higher than that in the face-centered cubic lattice; so twinning by a faulting process during growth with little change in boundary energy may be a possibility in copper and other face-centered cubic metals even when strain energy is not present. The dependence of the secondary recrystallization texture on manner of deforming the stable cube texture matrix, which the authors found, is much easier to explain by a nucleation process than by growth alone. Incidentally I should like to suggest similar experiments be done on single crystals rather than the cube texture material to test these findings on orientation changes during recrystallization.

On the other hand, there are two points of interest regarding the growth hypothesis. If the "off-orientation" grains finally disappear from the matrix with sharpening of the cube texture, then the matrix should become stable on the basis that sameness of orientation does not favor growth. Straining such a matrix, of course, would initiate a recrystallization process. Secondly, the precise relationship found between secondary twin pairs and the cube texture could be accounted for in terms of recrystallization of the cold-rolled structure. This would arise from recrystallized grains having the  $38^\circ$ - $22^\circ$  relationship with respect to a (100) [001] weak component of the cold-rolled texture. Such a component of the cold-rolled texture has been reported by Burgers<sup>5</sup> and others. The origin of larger grains having the (001) plane common with the (100) [001] texture might be similarly explained; their origin does not appear to reside with twins or twin faults in a nucleation process.

The authors point out a number of interesting things in connection with coincidence plots and suggest that such plots may be useful in the analysis of recrystallization data in silicon iron. If such plots have to be made with reference to the active plane—{111} or {100} in FCC lattices—as the authors have done, then I can understand their suggestion of using the {110} plane for the silicon-iron lattice. Recrystallization in silicon-iron crystals, which were deformed a small amount, occurs according to a sub-set of third-order twins.<sup>19, 28</sup> These have a  $\langle 110 \rangle$  axis common with the

parent crystal. Somewhat less accurately, the relationship is that of second-order twins and all such twins have one  $\langle 110 \rangle$  axis in common with the parent grain. On the other hand, it seems to me that the {112} plane, which is the twinning plane, would be just as good for a coincidence plot. Barrett<sup>11</sup> believes that twins of minimum thickness or twin faults form in ferrite during deformation. Twins are always in good coincidence; so small atomic movements would easily permit an orientation change from first to second-order twins and this would appear as a rotation about an appropriate  $\langle 110 \rangle$  axis. In any case I would be happy to see coincidence plots applied to BCC lattices.

There is an effect of orientation on ease of growth as well as one of ease of regrouping at the initial stage of a nucleation process, because nucleation requires sufficient growth to pass the energy hill. This latter aspect of the problem, which is concerned with finding the role played by orientation relationships in all growth processes, is, I believe, a very important one at the present time.

W. M. BALDWIN, JR.—I agree with, and should like to support, the authors' findings anent the orientations obtained on annealing rolled cubically aligned copper strip.

The limitation which the authors place upon their observations, "The importance of the observation that the orientations of the grains resulting from the recrystallization of the rolled (cubically aligned) samples are essentially insensitive to the degree of rolling cannot be overemphasized, for it indicates the action of a fundamental, discrete mechanism of deformation and recrystallization throughout the range of deformation studied," is quite judicious. At higher reductions, of course, the orientations resulting from annealing have been reported to be quite different.<sup>12</sup> When cubically aligned copper is rolled 81 or 91 pct and then annealed, a structure closely approximating a (110)  $[1\bar{1}2]$  texture results. *If cubically aligned copper is rolled 50, 60.5, or 72 pct, and then annealed however, a mixture of two discrete orientations is found: one orientation being that which the authors report for cubically aligned copper that is rolled in the range 0 to 35 pct, and then annealed, the other being (110)  $[1\bar{1}2]$ .* It thus appears that there are a number of discrete orientations which appear on recrystallization, each developing successively as the strain within a specific region increases. A clue of extreme significance in this mystery is the fact that the second orientation represents almost exactly twice the strain of the first on a crystallographic basis—if the mechanism of deformation described in reference 12 for rolling cubically aligned strip is accepted.

J. E. BURKE—The authors mention in their paper, and there have been mentions repeatedly in the literature, the several reorientations that can occur on secondary recrystallization: The rotation about a (111) pole, rotation about a cube pole, and possibly, rotations about other poles that are not too well defined. Do they have any information as to the exact conditions which may give rise to the one or the other of these various reorientations?

J. S. BOWLES—I had intended to ask the question which Dr. Burke just asked. We had the experience in Melbourne that some single crystals of copper produced by secondary recrystallization possessed an orientation which was related to the "cube structure" by a rotation about the (100) direction rather than the (111) direction. The copper was the same as we had used in our work on secondary recrystallization, and the amount of reduction and annealing temperature were similar. Information regarding the conditions under which these different rotations were produced would be of value.

M. L. KRONBERG and F. H. WILSON (authors' reply)—We thank all of you for these stimulating discussions. In particular, we are indebted to Dr. Mathewson for his enriching contribution of so much



new information, as well as for his appreciative evaluation of the work.

Dr. Mathewson has analyzed the crystallography of the  $22^\circ$ - $38^\circ$  coincidence plot, and further elaboration on this subject is in order. Referring to fig. 13, he has shown that directions of the form  $\langle 213 \rangle$  can be superposed by rotating either  $22^\circ$  in one direction or  $38^\circ$  in the opposite one. The directions under consideration are defined by the sides of the unit multiple triangular net defined by the coincidence points. Examination of the figure shows that one orientation can be derived formally from the other by a  $180^\circ$  rotation about such a line. As has been pointed out to M. L. Kronberg by J. D. H. Donnay, such a rotation is a twinning operation, and therefore it is appropriate to speak of the corresponding orientation change as occurring by twinning. At right angles to such a twinning axis there is a mirror plane of symmetry which bisects an angle of the unit multiple triangular net.

Considering the two dimensional plane interfaces used in constructing figs. 12 and 13, one can see no composition plane common to the two orientations. As Dr. Smith has pointed out, it might be advisable to consider an appropriately warped three dimensional interface in order to make the two lattices completely coherent and continuous. This has not been done to date, but it should be pointed out that the multiple lattice is common to the two orientations.

Dr. Mathewson's analysis of the origin of the annealing twins formed from the lightly rolled, cubically aligned copper free of twins is particularly significant—not only because of the very nice results—but also because of the method employed. The analysis rationalizes both the origins and orientations in terms of a mechanism of plastic deformation. This is a particularly important type of analysis, for it is clear that the eventual goal, in studying plastic deformation, strain hardening, recrystallization and softening, is to obtain a unified picture relating all these phenomena.

With respect to this kind of analysis, we wish to refer briefly to a particular time experiment of Neng-Kuan Chen, reported in his doctorate dissertation.<sup>20</sup> A tapered single crystal of aluminum, designated as A-2, was axially elongated, and the resulting orientation changes along the length of the specimen were documented by back-reflection Laue photographs. The sample formed deformation bands, but it was found that they were regions which lagged behind the bulk of the crystal as it underwent orientation changes. Otherwise, the changes for the bulk of the sample were found to be in accord with the classical analysis of Taylor and Elam, i.e., the slip direction moved along the great circle common to the specimen axis and the slip direction an amount determined by the induced shear. In fig. 28, which is a reproduction of Chen's fig. 56a,  $P_0$  and  $P_1$  are the initial and final positions of the specimen axis for the narrowest end of the tapered section. On recrystallization, this portion of the sample developed a highly oriented texture. The orientations of twenty-five of the grains are shown in the figure, and it is seen that they are simply related to the parent by a  $37^\circ$  to  $40^\circ$  rotation about the active cross-slip pole.

As Dr. Beck points out, there are two apparently conflicting viewpoints as to the origin of such a recrystallization texture. (1) The new grains form directly from stressed portions of the deformed crystal by a process of oriented nucleation and subsequent oriented growth of stress-free crystals involving an atomic rearrangement of the kind illustrated by the coincidence plots of figs. 12 and 13 in this paper. For this case the driving force for the reorientation would be the residual stress of the deformed metal. (2) The new grains originate by a process of oriented growth alone of fragments produced during the plastic deformation. How such stressed fragments could produce stress-free crystals on growth has not been clearly analyzed, but one might hypothesize that a bent one

could yield stress-free units by polygonization, a stress-free unit thus being the one that grows.

It seems that the experiment just described is very strong evidence in favor of the nucleation mechanism (1) because one obtains an answer which is very straightforwardly related to the process of plastic deformation, at least as we understand it today. In order to give credence to the second possibility, one must conclude that the process of plastic deformation has not only produced the experimentally observed orientation change  $P_0 \rightarrow P_1$ , but has also produced fragments—as yet undetected by direct experiment or predicted by theory—which are related to  $P_1$  by a massive rotation of  $37^\circ$  to  $40^\circ$  about the cross-slip pole. Since there is no current way of understanding

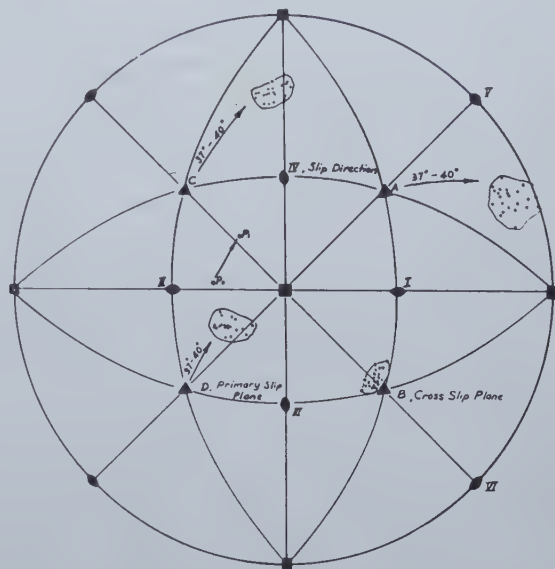


Fig. 28—Chen's figure showing orientation relationships for axial elongation and recrystallization of an aluminum single crystal.

how such hypothetical fragments might originate, and since a simple answer is derived from hypothesis 1, it can be concluded that the evidence favors the oriented nucleation hypothesis for this type of experiment. Similar experiments susceptible to the same kind of argument are referred to earlier in this discussion, i.e., the Kronberg and Wilson recrystallization study of lightly deformed cubic copper, the experiments on single crystals of brass reported by Maddin, Mathewson and Hibbard,<sup>30</sup> and those of Turkalo and Turnbull<sup>25</sup> on lightly strained cubically aligned copper.

On the other hand, it is important to realize that there is nothing in this kind of argument which discredits the oriented growth hypothesis for experiments which produce a suitable heterogeneity of orientations during the plastic deformation. For such a case, the oriented growth mechanism could operate exclusively, or it might operate in competition with the oriented nucleation one. This brings us to the apparent conflict, as pointed out by Dr. Beck, in the interpretations of the Kronberg and Wilson, and Beck and Hu experiments.

First, Dr. Beck points out that many of the experimental results reported in the Kronberg and Wilson paper are in excellent agreement with those observed independently and published practically simultaneously by Beck and Hu, and Rathenau. In order to avoid the possible misunderstanding that Dr. Beck implies that some of the experimental results are not in agreement—and we do not think that such is Dr. Beck's intention—it should be pointed out that the experiments performed by the three groups of investigators were really different although similar in



many respects and were performed on chemically and physically different kinds of materials. Apparently there is no reason to question the validity of any of the experimental findings. Rather, we are to recognize that a variety of experiments on recrystallization and grain growth yields similar kinds of orientational relationships between recrystallized (or coarsened) and parent grains. With the possible exception of the one experiment already discussed here on the recrystallization of the lightly deformed cubic copper, there is nothing completely unambiguous about the experiments which permits one to interpret the results exclusively in terms of either the nucleation or growth mechanisms, although the various authors point up various arguments in favor of one or the other of the interpretations. A good service rendered by Dr. Dunn is his emphasis of this point by his comments which show that either (or both) interpretation can account for the experimental observations. One can conclude that the experiments to date do not resolve the controversy over the nature of secondary recrystallization, or coarsening, and that we must appeal to additional effort for a possible better understanding of this subject. The evidence given earlier in the discussion however does suggest a kind of circumstance under which oriented nucleation could occur during primary recrystallization. To come to any one exclusive answer for the mechanisms of primary and secondary recrystallization at this time, when our knowledge of plastic deformation and recrystallization is still imperfect, would only cripple the pursuit of increasing enlightenment through new experimentation and fresh thinking.

Returning to Dr. Mathewson's discussion, he has pointed out in his analysis of the origin of recrystallization twins that it is not possible to convert a twin-fault into a pair of annealing twins by the rotational mechanism which we have discussed. Modifications are required, and he has developed appropriate ones so as to give a possible mechanism for the phenomenon.

Dr. Dunn has presented information concerning self straining on annealing and points out that strains of this type might promote nucleation during secondary recrystallization. There certainly can be no objection to this suggestion.

In addition, he refers to his work on the recrystallization of lightly deformed silicon ferrite and points out that the new grains can be related to the parent by bulk rotation about  $\langle 110 \rangle$ , which is the active slip plane for this material. This is quite analogous to our work on lightly deformed, cubically aligned copper in the sense that the new grains can be related to the old by rotations about the pole of an active slip plane.

We have not had an opportunity to date to explore his suggestion of applying coincidence plots to a  $\{112\}$  twinning plane as a possible plane of rotation.

Dr. Baldwin has pointed out the results of orientation studies of recrystallization following higher deformations than those which we covered. It might have been expected that, since the deformation texture up to the 35 pct reduction involves comparatively little spreading of the cubic orientation, recrystallization of the more complicated deformation textures following 60 to 90 pct reduction would give even more complicated textures than a simple mixture.

With respect to Dr. Beck's comments concerning the purity of the materials used in our work, it is pertinent to record that we repeated many of our experiments with samples made from A.S. and R. super purity copper and obtained confirmatory results. Twin bearing, cubically aligned samples underwent secondary recrystallization; twin-free ones did not unless they were lightly deformed.

Dr. Burke and Dr. Bowles have inquired about the conditions which produce orientations during secondary recrystallization other than the rotations about  $\langle 111 \rangle$ . All that we know about the conditions which

produce  $\langle 100 \rangle$  rotations in copper is recorded in the paper. Some additional comments can be made by Kronberg on some experiments on Fe-Ni alloys done by him in the Hammond Laboratory. Apparently, pure nickel and an alloy containing around 20 pct iron behave similarly to copper. The rotations during secondary recrystallization are almost exclusively about  $\langle 111 \rangle$ , and only infrequently about  $\langle 100 \rangle$ . For alloys containing around 50 and 65 pct iron, the situation is reversed. In addition, for the 65 pct iron alloy, one also observes the orientations found by Rathenau, which are not related to the parent by rotation about either  $\langle 111 \rangle$  or  $\langle 100 \rangle$  poles. We have here the interesting observation that a change in composition of a phase alters the nature of the secondary recrystallization in the material. Accompanying the composition change, there is of course an associated change in the elastic constants, but it is not known whether the alteration in the recrystallization behavior can be attributed to such a change.

The strongest objection voiced to date to our suggestions concerning oriented nucleation and coincidence plots is the claim that it is not necessary to resort to them to explain experimental observations. We take the attitude that our understanding of the phenomena of recrystallization could be simplified by the application of the coincidence plots, and that this promise presents a challenge to acquire critical evidence to evaluate their applicability. Extensive reorientations do occur during recrystallization after deformations which are so light that the possibility of rotation of fragments to the new orientation eventually observed after recrystallization seems highly improbable. The mechanism described in this paper is presented as one possible means for accomplishing extensive rotations without extensive atomic displacements.

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# Recovery and Recrystallization in Brass

by B. L. Averbach

DISCUSSION, W. R. Hibbard, Jr. presiding

C. S. BARRETT—The X-ray diffraction measurements in this investigation and in the related ones at M.I.T. are, I believe, among the most accurate that have ever been made. There is still a possibility, however, that important details of the cold-worked state will be missed if it is always assumed, as I believe it is assumed here, that reciprocal lattice points are broadened equally in all directions by cold work. Since anisotropic broadening of points has been found from various types of disorders in crystals, it would be desirable to have measurements on cold-worked and on recovered single crystals. Is there a plan to continue the work using single crystals?

It is curious that there is so little change in extinction during annealing in the recovery range. There are changes of some sort, of course, since hardness changes. If "polygonalization" played any part in the recovery of brass it would seem that clear evidence of it would have been found in these data.

C. S. BARRETT, University of Chicago, Chicago, Ill.

B. L. AVERBACH (author's reply)—We recognize the limitations of the powder pattern technique, and are at present studying the distribution of intensity in reciprocal lattice space for deformed brass crystals. The results are too preliminary to be discussed now.

## Recrystallization Texture and Coarsening Texture in High Purity Aluminum

by P. A. Beck and H. Hu

DISCUSSION, J. E. Burke presiding

F. H. WILSON—The authors have shown very nicely that the recrystallization texture of rolled or compressed single crystals of aluminum, and the orientations of coarse grains growing in the recrystallized matrix, can be derived from their respective parent structures by rotations about  $[111]$  poles. However, they attach no more significance to this derivation than to say that the deformation makes nuclei of a favorable orientation available. The "oriented growth" theory then goes on to state that recrystallization textures, and the orientations of coarse grains, result from the preferred growth of these nuclei of favorable orientation.

I would be the last to deny the orientation dependence of rate of growth in a matrix having a preferred orientation, but I cannot accept the belief that "oriented growth" determines the resulting preferred orientation. Some of the textures studied in this neat group of experiments are more sharply defined than one could expect from "oriented growth" alone. For instance, "oriented growth" has allowed an extensive range of orientation to grow in a "sharply defined" recrystallization texture in the case of Crystal II. However, if it alone determined the preferred orientation, one could hardly expect the sharp textures, both in recrystallization and coarsening, which are found in Crystal I. The authors state that the observed derivations of textures "do not prove that nuclei of other orientations do not exist," but I am inclined to believe that the derivation of a sharp texture from a sharp texture is strong evidence that only nuclei of the new orientation are present. However, these "nuclei" are not the three-dimensional units to which the term "nucleus" customarily refers. Rather, as described in the first paper presented at this session,<sup>20</sup> they are two-dimensional embryos of nuclei existing at regions of somewhat higher energy in the parent lattice.

I would take issue with the authors' statement that "It may be assumed that in a recrystallized material, even with a strong texture, there always are present some grains of practically any orientation." This is a premise of the "oriented growth" theory. Anyone who has looked at the structure of twin-free cubically aligned copper would have to discard all evidence that grain growth proceeds under the influence of surface energy forces to believe that any small nucleus of a strange orientation can exist therein. Indeed, I believe that strange orientations cannot exist in undetectable amounts in a recrystallized matrix—their surface curvatures would be too great.

It is, of course, gratifying to Mr. Kronberg and myself to find that Crystal I shows rotations around  $[111]$  within  $\pm 4^\circ$  of  $38^\circ$  both on recrystallization and coarsening, and similar results in the authors' re-interpretation of the data of Burgers and Louwse<sup>6</sup> on recrystallization of a compressed single crystal. Our own re-interpretation<sup>20</sup> of the data of Barrett<sup>8</sup> and of Bowles and Boas<sup>15</sup> found an angle of  $38^\circ$  to be significant. We also drew a coincidence plot for rotations of  $28^\circ$  ( $32^\circ$ ) and this may be significant in interpretation of the  $27^\circ$  and  $33^\circ$  rotations which the authors find in the data of Burgers and Louwse<sup>6</sup> for recrystallization of a rolled single crystal. The results of two other experiments are given in the authors' table III. Because of the spread in orientations, little can be said about Crystal II. However, at the risk of giving the impression that a coincidence plot can be pulled out of the hat for any observed rotation, I would like to say a little about the  $47^\circ$  rotations during recrystallization of Crystal III. In the family of  $(111)$  coincidence plots, the  $38^\circ$  ( $22^\circ$ ) rotation has the greatest density of coincidence sites; the next most dense is  $28^\circ$  ( $32^\circ$ ). In our paper we did not include any higher angles than  $38^\circ$ , but the rotation corresponding to the third greatest density of coincidence sites is  $47^\circ$  ( $13^\circ$ ). For the present I do not claim anything more than that the equivalence of rotation of Crystal III and this  $47^\circ$  plot is coincidental. However, the simplicity of atomic motions involved in a  $47^\circ$  coincidence plot is of interest. This plot is shown in fig. 18. At the left, atoms in a single plane are shown before (open circles) and after (filled circles) the effective  $47^\circ$  rotation. At the right, the motion of atoms in three planes is illustrated—small circles in the plane below and large circles in the plane above the original plane. Note that each atom moves only  $13^\circ$  around the coincidence site in its plane in an opposite direction from that of the effective bulk rotation. The longest path is no more than  $\frac{1}{2}$  an atomic distance.

Finally, I would like to ask if the authors feel that the single recrystallization texture is developed in both the main portion of the deformed material and the deformation bands, or that the recrystallized grains from the main portion have absorbed the material of the deformation bands whether before or after it recrystallizes?

F. H. WILSON, Technical Department, The American Brass Co., Waterbury, Conn.

P. A. BECK and H. HU (authors' reply)—In answer to Dr. Wilson, I would like to review again, briefly, the present status of our thoughts on texture theory. The work of Bowles and Boas,<sup>15</sup> of Rathenau and Custers,<sup>27</sup> of Kronberg and Wilson<sup>20</sup> and the present paper furnish ample corroborative evidence for the predominance in various face-centered cubic metals of a certain orientation relationship (rotation of  $30^\circ$  to  $40^\circ$  around a  $[111]$  axis) between grains growing in a matrix with a strong single orientation texture and the matrix itself. It is furthermore definitely established that this orientation relationship is essentially the same in both *recrystallization*, when the matrix is a cold-worked single crystal and the growing grains are essentially strain free, and in *coarsening* when both the fine-grained highly oriented matrix and the growing grains are essentially



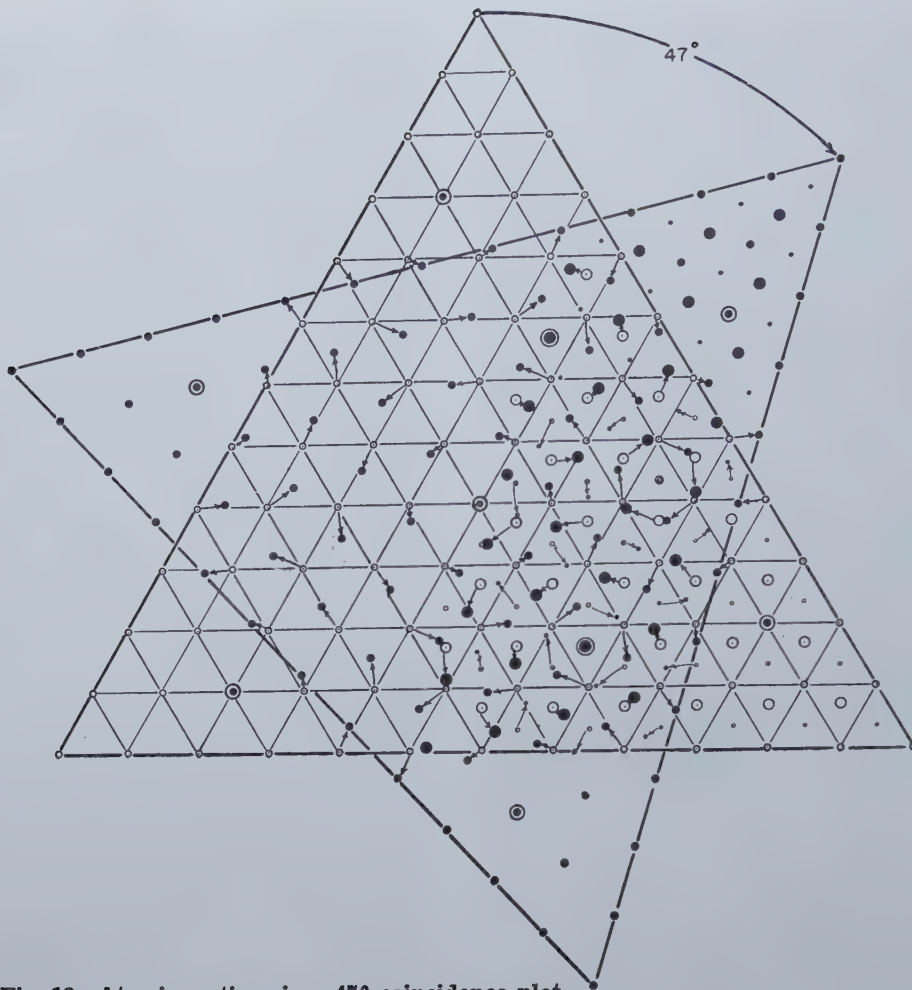


Fig. 18—Atomic motions in a 47° coincidence plot.

strain free.\* Since the driving force of grain boundary migration in the first case may be as much as 100 to 1000 times larger than in the second case, the identity of the orientation relationships in these two processes is truly remarkable.

\* The use of the term *recrystallization* in this specific sense ("primary recrystallization" in cold-worked metals) has been quite generally accepted in the technical literature of English speaking countries. The term *coarsening* has been widely used in the steel industry for many years to describe the discontinuous type of grain growth denoted by certain investigators as "exaggerated grain growth" or "abnormal grain growth." However, the latter terms have been used also in reference to recrystallization after small deformations ("critical recrystallization"); therefore, they may be misleading. The term "secondary recrystallization" is unsuitable because it implies that the phenomenon is strain induced (see ref. 26) — a highly questionable proposition.

This re-orientation, occurring whenever a new generation of grains is growing in a highly oriented matrix, might conceivably come about in one of two ways. One may assume either, as Kronberg and Wilson do, that nuclei for the new grains are available *only* in the required orientations ("oriented nucleation") or, as we do, that from among available nuclei of a great variety of orientations those with suitable orientation relationship with respect to the matrix have by far the highest rate of growth ("oriented growth") and will, therefore, predominate. In addition to the work of Dunn,<sup>25</sup> independent observations made by Rathenau and Custers,<sup>27</sup> Kronberg and Wilson, and ourselves on coarsening, artificially nucleated at points of heterogeneous local deformation, make it quite certain that in coarsening the rate of growth is in fact orientation dependent. The selective growth of grains having the correct orientation with respect to the matrix, when "nuclei" of a large variety of orientations have been provided artificially (fig. 19), cannot be rationalized without accepting the fact that the rate of growth in coarsening is orientation dependent. Furthermore, the three investigations just

mentioned all contain data to prove that the *orientation corresponding to the highest rate of growth is the same as found in textures produced by spontaneous (not artificially nucleated) coarsening*. More recently it was possible to prove<sup>28</sup> that the same is true in the case of artificially nucleated recrystallization (fig. 20). Once it is clearly understood that the experimental facts can be readily accounted for on the basis of oriented growth—itsself an experimental fact—the hypothesis of oriented nucleation is obviously unnecessary. It should be pointed out also that oriented nu-



Fig. 19—Orientation dependence of the rate of boundary migration in coarsening.

Several small grains of varying orientation produced by annealing at the sheared (lower) edge of the specimen. From among these "nuclei" those with favorable orientation grew large at the expense of the fine-grained matrix of single orientation texture. This matrix was produced by a 3 min anneal at 525°C of a high purity aluminum single crystal, previously rolled to 90 pct reduction of area. Deep etching. X8. Area reduced approximately one sixth in reproduction.



cleation by itself is incapable of accounting for the experiments with artificial nucleation, referred to above.

It is well known that textures obtained by coarsening are usually much more sharply defined than the original matrix texture from which they developed. For instance the (110) [100] texture in silicon-iron is formed by coarsening from a recrystallized matrix with a rather weakly developed texture.<sup>25</sup> It is easy to see that the sharpening of the texture in coarsening cannot be accounted for on the assumption of oriented nucleation. On the basis of that hypothesis, the orientation of individual nuclei might be very accurately related to the orientation of the individual matrix grains in which they formed. Even then, this would lead to a spread in the coarsening texture at least equal to that in the matrix texture. On the other hand, if the coarsening texture results from oriented growth, and the rate of growth of the coarse grains is determined by their relative orientation with respect to the average orientation of the neighboring small matrix grains, much of the orientation scatter present in the matrix will be eliminated from the coarsening texture. Thus the observed sharpening of the texture in coarsening is easily interpreted on the basis of oriented growth.

Kronberg and Wilson<sup>26</sup> state that, "The positive result that 'secondary recrystallization' does not occur in twin-free cubically aligned copper but does in twin-bearing material . . . is the strongest kind of experimental evidence in favor of the concept of nucleation of new orientations at twin boundaries in the cubically aligned material." Their failure to produce spontaneous coarsening in cubically aligned aluminum was cited by Kronberg and Wilson as additional evidence in favor of the specific brand of oriented nucleation theory, which requires the presence of twin boundaries for the occurrence of a nucleation event. This theory cannot explain the results of the present investigation, which indicate that coarsening in fact does occur in fine-grained high-purity aluminum of a single orientation texture. It is significant that, according to Kronberg and Wilson's observations, the twin-free cube texture in copper is more perfectly developed than the "cube component" of the twin-bearing material. It appears very probable that the occurrence of spontaneous coarsening in the twin-bearing material is a result of the presence of a sufficient number of grains suitably disoriented with regard to the main texture to serve as "nuclei" for coarse grains. Similarly, the slowness of spontaneous coarsening in the twin-free material may be attributed to the more sharply defined texture which does not contain large enough grains with orientations sufficiently deviating from the main texture. When "nuclei" with such off-orientations are provided by inhomogeneous local deformation and recrystallization, coarsening quickly proceeds. This interpretation is again in good agreement with the work of Rathenau and Custers<sup>27</sup> who showed that in a face-centered nickel-iron alloy with cube texture spontaneous coarsening occurs within a certain range of perfection of the cube texture. If the perfection of the texture becomes too great (after too high deformation), spontaneous coarsening no longer occurs in the range of annealing conditions used, but, here too, coarsening can be induced by providing grains of off-orientation by recrystallization after an inhomogeneous local deformation.

As discussed in ref. 28, the evidence now available convincingly shows that, even in the presence of ample driving energy, low-energy grain boundaries, corresponding to nearly identical or nearly twin orientation, migrate very reluctantly. On the other hand, high-energy grain boundaries, such as those between grains of a relative orientation corresponding to a [111] rotation of about 30° to 40°, are highly mobile. It is possible that grain boundary migration takes place by a mechanism requiring self-diffusion along

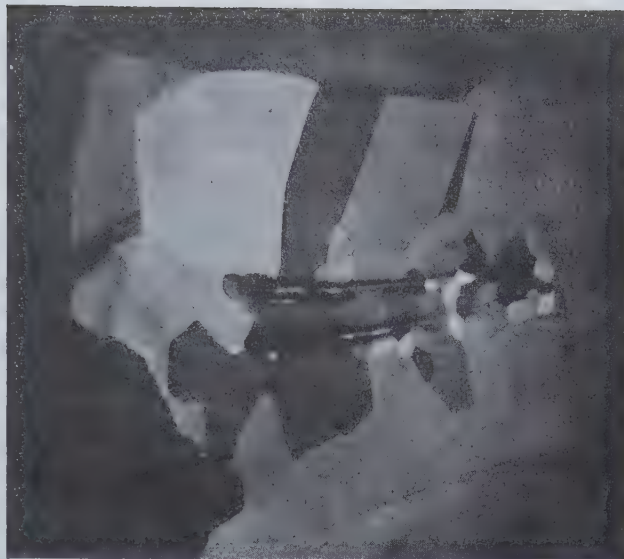


Fig. 20—Orientation dependence of the rate of boundary migration in recrystallization.

Many small recrystallized grains of various orientations formed at the immediate vicinity of the two scratches. Those recrystallized grains with suitable orientation with respect to the cold-worked matrix grain grew selectively. High-purity aluminum initially annealed 4 hr at 650°C, rolled 12 pct, electrolytically polished and scratched, annealed 1 hr at 350°C. Repolished and anodically etched. The two scratches were partially removed by repolishing in order to make the numerous small grains more clearly visible. Polarized light, Biot-Klein quartz plate. X25. Area reduced approximately one sixth in reproduction.

the migrating grain boundary. If so, the low mobility of low-energy boundaries and the high mobility of high-energy boundaries could be a result of the low, respectively high, rate of self-diffusion along such grain boundaries.

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### Recrystallization and Microstructure of Aluminum Killed Deep Drawing Steel

by R. L. Rickett, S. H. Kalin, and J. T. MacKenzie, Jr.

DISCUSSION, J. E. Burke presiding

J. E. BURKE—I am particularly intrigued by the effect of cooling rate of the steel prior to the final reduction upon the course of the recrystallization process which occurs later. Mr. Rickett finds that slow cooling from 1500°F causes aluminum-killed steel to behave similarly during recrystallization to rimmed steel, while rapid cooling leads to slower recrystallization and typical pancake-shaped grains. I should like to point out that there is considerable evidence that the role of the cooling rate, and of the other early thermal treatments, is probably to control the size and distribution of the inclusions which can inhibit grain boundary migration. M. L. Samuels<sup>4</sup> has observed that exaggerated grain growth occurs in certain mild steels only after proper cooling rates preceding the final box anneal. Similarly, I have observed<sup>5</sup> that the rate of grain growth in alpha brass can be profoundly influenced by the rate of cooling from high temperature prior to a final cold reduction and recrystallization. In these cases, the observations are consistent with the explanation that at least some second phase inclusions



go into solution during the heating. If the specimen is rapidly cooled they reprecipitate in highly dispersed form which efficiently restricts grain boundary migration, while if the specimen is slowly cooled, time is available for diffusion over greater distance, so the final precipitate consists of a smaller number of larger particles which have less effect upon grain boundary migration. This explanation is also consistent with the fact that slow cooling makes killed steel behave more like rimmed steel during recrystallization. One thing bothers me however, and I should be interested in Mr. Rickett's comments on it. He has observed that growing recrystallization nuclei have difficulty in crossing the old grain boundaries if the steel originally was cooled rapidly, while less difficulty exists if the steel was cooled slowly, as in the rimmed steels. One would expect, however, that during slow cooling the precipitating phase would have more chance to form at the grain boundaries, and thus that pancake-shaped grains would be more likely to form in slowly cooled material. Possibly coalescence is sufficient with slow cooling so that the inclusions have little effect upon grain boundary migration, and that during rapid cooling there is still sufficient preference of the precipitate for the old grain boundaries so that the new grains have difficulties in crossing them.

J. E. BURKE, *Knolls Atomic Power Laboratory, General Electric Co., Schenectady, N. Y.*

R. L. RICKETT (authors' reply)—As suggested by Dr. Burke, there may be sufficient precipitation at grain boundaries during rapid cooling to inhibit recrystallization and grain growth after subsequent cold reduction, whereas after slow cooling the precipitated particles may be too large to be effective. An alternative explanation for inhibition at former grain boundaries is that the inhibiting material is retained in solution when the steel is cooled rapidly, and then is precipitated during heating after cold reduction.

#### References

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## The Crystal Structure of Ni<sub>4</sub>W

by E. Epremian and D. Harker

DISCUSSION, C. H. Samans presiding

R. M. TRECO—The present paper gives rise to several interesting theoretical points, particularly if we consider also the analogous compound Ni<sub>4</sub>Mo which has a crystal structure identical to that of Ni<sub>4</sub>W. A consideration of the work of Hume-Rothery and others leads one to expect intermetallic or electron compounds when the electron:atom ratio exceeds about 1.40 and the size factor is unfavorable. Superlattices, on the other hand, are characterized by the simple ratios AB and A<sub>2</sub>B in most cases because these compositions usually indicate zone transitions. Combination of a size-factor which is favorable yet not too favorable and a high zone number for the solute atoms is observed in ordered atomic arrangements. The electron:atom ratio is 0.40 for Ni<sub>4</sub>W and 0.20 for Ni<sub>4</sub>Mo, neither of which can be made to satisfy the usual ratio requirements for electron compounds even if a substitution of electrons for atoms in various ratios is made as suggested by Norbury. However, the ratio Ni<sub>4</sub>W is close to that of the A<sub>2</sub>B superlattice type and a consideration of the closest distance of approach of the

R. M. TRECO, *Massachusetts Institute of Technology, Cambridge, Mass.*

Ni and W atoms for the observed structure shows the following:

Each of the body-centered W atoms has:

4	Ni neighbors at	1.866 Å
4	Ni neighbors at	2.469 Å
4	Ni neighbors at	2.561 Å
8	W neighbors at	3.371 Å
2	W neighbors at	3.553 Å
4	W neighbors at	5.730 Å

and it is apparent that this satisfies the conditions for a fourth-zone superlattice in respect to nearest solute neighbors (the same is true for Ni<sub>4</sub>Mo except that the distances are just slightly different). The size-factor is just within the acceptable range for Ni and W or Mo. Other considerations are that the compound Ni<sub>4</sub>Mo has been shown previously to be a superlattice, and that the resistivity of the  $\beta$  phase is not exceptionally high when compared with pure metals and some alloys, since alloying increases resistivity as does the presence of quenching stresses. The authors point out that the drop in resistivity on aging is greater for the 19.8 at. pct alloy which is closest to the ideal ratio, Ni<sub>4</sub>W. Alloys which equal or slightly exceed this ratio in W may have even lower resistivity with similar aging treatment.

Since the mechanism of the change to  $\beta$  structure is temperature dependent, appearing to be a phase change above 950°C, yet definitely establishing itself as an ordering reaction below this temperature, it would seem logical to designate the alloys below 950°C as  $\beta'$  as has been done in the Cu-Zn system.

Have the authors found a similar temperature-dependence in the mechanism of the reaction for the 17.6 at. pct W alloy and, if so, did the mechanism also change at 950°C? In order to establish the upper limit of the proposed  $\beta'$  phase in this system, information on the temperature at which the reaction mechanism changes for other alloys in this range should be interesting.

E. EPREMIAN and D. HARKER (authors' reply)—An ordered structure may be—and has been—defined as one in which atoms have essentially the same relative positions as in a solid solution, but in which the different atomic species are arranged in an orderly way. In this sense, both Ni<sub>4</sub>W and Ni<sub>4</sub>Mo have ordered structures based on the face-centered cubic structure of the solid solutions of W and Mo in Ni. An ordered structure may form as a separate phase—by the nucleation and growth of a precipitate, for instance—or by a homogeneous reaction—"ordering." In the case of Ni<sub>4</sub>W, it has been shown that the same structure can form by both mechanisms. However, it does not seem reasonable to change the name of a substance, depending on the method of its preparation. Consequently, the distinction between  $\beta$  and  $\beta'$  proposed by Treco appears unrealistic.

Treco's table of interatomic distances is incorrect. The Ni neighbors of a W atom are: 8 Ni at 2.538 Å, 4 Ni at 2.563 Å.

The experiments suggested by Treco on the temperature dependence of the mechanism of formation of 17.6 at. pct W in Ni have not been carried out, and it seems unlikely that an opportunity to do this work will arise.

## Structure of Diborides of Titanium, Zirconium, Columbium, Tantalum, and Vanadium

by J. T. Norton, H. Blumenthal, and S. J. Sindeland

DISCUSSION, R. L. Rickett presiding

R. KIESSLING—This paper is of interest to those of us who are working on borides of transition elements. For CrB<sub>2</sub>, which is of interest in this connection, we at Uppsala have obtained the following values for the lengths of the axes<sup>2</sup>:

$$a = 2.969 \text{ Å}, c = 3.006 \text{ Å}, c/a = 1.033$$



Thus the calculated lattice dimensions will be (in Angström units)

	Metal to Metal in Sheet	Boron to Boron in Sheet	Metal to Boron	Separation of Sheets	Metal to Metal in Pure Metal
CrB <sub>2</sub>	2.97	1.72	2.30	3.07	2.56
Mo-B $\epsilon$ -phase	3.01	1.74	2.31	3.13	2.80
W-B $\epsilon$ -phase	2.98	1.72	2.34	3.07	2.82

No further decrease of the separation of the metal sheets is thus observed when going from vanadium to chromium. The binding between adjacent boron atoms may, however, cause a deformation of the spherical shape of the atoms.

It may be mentioned further that the  $\epsilon$  phases in the molybdenum and tungsten-boron systems are related to the MeB<sub>2</sub> phases discussed. They consist in part of simple hexagonal metal lattices with boron nets between the metal sheets. The values for the simple hexagonal parts of these phases are given above, but it must be pointed out that it is impossible to determine whether the boron nets are complete or not.

Our investigations on columbium and tantalum-borides have shown that CbB<sub>2</sub> and TaB<sub>2</sub> have extended homogeneity ranges. For TaB<sub>2</sub> the values are

Lower limit about 64 at. pct boron	66.7 at. pct boron	Upper limit about 72 at. pct boron
$a = 3.099, c = 3.224 \text{ \AA}$	$a = 3.078, c = 3.265 \text{ \AA}$	$a = 3.057, c = 3.291 \text{ \AA}$

The decrease of the  $a$ -axis and increase of the  $c$ -axis indicate that the hexagonal nets of boron atoms for higher content of boron than 66.7 at. pct are filled up by additional boron atoms in the centers of the already existing rings of the nets, giving more or less complete sheets of boron atoms. The extension of the homogeneity range to boron contents lower than 66.7 at. pct may be explained if the other phases of this system are regarded.<sup>6</sup>

Concerning the application of Hägg's rule for borides of the transition elements, we have come to the same conclusion as the authors. Studies on the borides of Th, Zr, Ta, Cb, Mo, W, Cr, Mn, Fe, Co, and Ni show that Hägg's rule is valid only if the boron atoms occupy isolated positions in the metal lattice. The boron atoms, however, have a marked tendency to form chains, nets or three-dimensional networks through the metal lattice and Hägg's rule seems not to be valid for these borides.

It is finally of great interest to note that conductivity measurements on ZrB<sub>2</sub> and TiB<sub>2</sub> have been made, and their metallic character confirmed.

R. KIESSLING, *Institute of Chemistry, University of Uppsala, Uppsala, Sweden.*

J. T. NORTON (authors' reply)—In our observations on columbium and tantalum boride we have observed that the diffraction lines were not sharp, whereas, for the other borides they were sharp. This suggested the possibility of a homogeneity range for these borides. Kiessling has confirmed that this homogeneity range is considerable.

I might also add that it is important to remember that in these interstitial structures the geometry is not the only thing to consider. With tungsten and molyb-

denum borides of the MeB<sub>2</sub> type, the radius ratio would be about 0.61, which would lie right in the range of the borides which we have been investigating. The fact that these elements do not form such borides is an indication that something about the chemical nature of tungsten and molybdenum is different from these other transition elements.

I do not quite understand Dr. Kiessling's statement that in the case of borides in which the composition exceeds that of the MeB<sub>2</sub> type that the extra boron atoms go in the center of these rings. If that is the case, it means that the boron atom must lie directly between two metal atoms which are practically in contact, and the only way I can make that picture agree is to imagine that perhaps there are vacancies in the metal atom sheet which permit the boron atoms to have these positions.

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## The Isolation of Carbides from High Speed Steel

by D. J. Blickwede and M. Cohen

DISCUSSION, R. L. Rickett presiding

L. C. CHANG—The authors are to be complimented on their paper describing in great detail the electrolytic extraction of carbides in high-speed steels by two methods: the elaborate double citrate cell and the simple hydrochloric acid cell. They concluded that the citrate cell has the experimental disadvantage, aside from its complexity, that portions of the matrix of high-alloy steels may not dissolve during the electrolysis and that the 1:10 hydrochloric acid cell is simple to operate and yields quantitative results.

We have been using a method, previously developed at Battelle Memorial Institute, which seems to combine the features of both methods described by the authors. The cell arrangement is very similar to fig. 3 of the authors' paper except that a 304 stainless steel cathode is used instead of the copper cathode, and that there is introduced between the anode and the cathode a heavy filter paper thimble to keep the anode and extracted carbides separated from the nascent hydrogen being evolved at the cathode during electrolysis. The electrolyte contains 60 g per liter of ammonium chloride and 160 g per liter of citric acid. The cells are operated at room temperature with a current density of about ¼ amp. per sq. in. A study of the pH as a function of the operating time showed that the electrolyte became essentially a buffered solution with a pH between 2 and 3. This permitted the dissolution of about 15 g of sample in 24 hr with a current efficiency of about 90 pct.

The chemical analyses of extractions made at two different times of a sample of Rex M2 analyzing C, 0.84; Mn, 0.22; Si, 0.27; Cr, 4.08; V, 2.03; W, 6.15; and Mo, 4.93 are compared with those of the authors' in the tabulation below. These show good agreement between the chemical compositions of residues extracted by the Crucible Steel Co. method and the authors' hydrochloric acid method.

### Comparison of Chemical Analyses of Electrolytically Extracted Residues from 6 W; 5 Mo; 2 V High-speed Steels by Two Methods

Method	Residue, Pct	C	Mn	Si	Cr	V	W	Mo	Fe	Total
Crucible Steel Co.	19.2	4.24	0.17	0.57	7.87	8.40	27.93	21.45	24.99	95.62
Crucible Steel Co.	20.1	4.20	0.22	0.61	7.83	8.55	27.93	21.58	25.41	96.33
Authors'	21.7	3.72			9.34	8.05	27.3	21.4		



The authors' description of a metallographic method differentiating the following carbides: MC,  $M_6C$ ,  $M_{23}C_6$ , is extremely interesting. We have tried the method on several high-speed steels, including the 18-4-1 grade. Annealed specimens of 18-4-1 electrolytically etched with 1 pct chromic acid show scattered small gray as well as black particles. However, diffraction patterns of electrolytically extracted residues from annealed 18-4-1 fail to show the MC carbide pattern. We are not quite sure whether the scattered small gray and black particles in 18-4-1 after the 1 pct chromic acid electrolytic etch are a true representation of the MC carbide, and hope that the authors of this paper can offer us a satisfactory answer.

L. C. CHANG, *Research Laboratory, Crucible Steel Co. of America, Harrison, N. J.*

D. J. BLICKWEDE and M. COHEN (authors' reply)—It is gratifying to note the agreement between our results and those obtained by Dr. Chang with a different isolation method on another heat of M-2 high-speed steel. This independent confirmation lends further support to the significance of electrolytic extractions.

Frank Kayser at M.I.T. has recently applied the etchants described in this paper to several commercial grades of high-speed steel, including 18-4-1, and the MC carbide has been found in all cases by means of the chromic acid (electrolytic) etch. However, the amount of MC in 18-4-1 is so small (1.3 pct in the annealed state and 0.3 pct after austenitizing at 2350°F) that it cannot be detected with certainty in the X-ray photographs of the extracted residues. On the other hand, the MC carbide can be detected by X rays in the extracted residues of steels with higher vanadium contents, such as 6-5-4-2, 6-5-4-4, and 0-9-4-2, and the chromic acid etch shows correspondingly more of this carbide in the microstructure.

It is more difficult to distinguish the MC carbide in 18-4-1 than in 6-5-4-2 because the  $M_{23}C_6$  carbide seems to be more readily attacked in the former than in the latter steel. However, a freshly prepared 1 pct chromic acid solution used electrolytically at 2 v yields fairly positive results. The MC etches quite dark with virtually no attack on the  $M_{23}C_6$ . If the structure becomes somewhat overetched, the  $M_{23}C_6$  particles turn gray, as observed by Dr. Chang. Only the very dark particles are considered to be MC.

## Oriented Arrangements of Thin Aluminum Films on Ionic Substrates

by T. N. Rhodin, Jr.

DISCUSSION, W. L. Fink presiding

G. W. JOHNSON—Would the points of contact between the probes and the film affect its nucleation, growth and orientation? Were the diffraction measurements made after the film was cooled to room temperature and, if so, might the cooling stresses lead to some disorientation? Were any of the films stripped and heat treated independently of the substrate or were they all heat treated on the substrate?

T. N. RHODIN (author's reply)—First of all, with respect to the influence of the apparatus, itself, on the orientation, that is, the manner of suspension of the specimen, there were two platinum points, in contact with the specimen on the outer edges, between which the film was deposited, giving an index of the fact that the film was going down. The effect of the probe as a point of nucleation was not investigated, specifically. It does not seem too likely that such point would be an important influence on film growth.

With respect to the X-ray technique, the X-ray patterns were obtained at room temperature. The specimens were taken out and put into the camera. There is the possibility, certainly, of strain.

However, the fact that some high degree of orienta-

tion specific to each substrate was obtained indicates that the orientation was not due to the strain, but rather to the substrate. At least, that seems a very reasonable assumption.

Now, with regard to the X-ray technique, there is a question about this method. We do not know how good a single crystal surface we had. You see, there were steps in the cleavage surface. You could get a group of specimens having the same counter-axis growing at right angles to the surface on neighboring steps, so that it would appear as a highly oriented film. It would be a highly oriented film, with one question remaining about the film axis.

As far as heat treatment was concerned, no striking disorientation effect was observed upon cooling in vacuum. Most of the films were too thin to strip from the substrate for independent examination.

G. W. JOHNSON, *Department of Physics, Brookhaven National Laboratory, Upton, L. I., N. Y.*; E. A. GULBRANSEN, *Westinghouse Research Laboratory, East Pittsburgh, Pa.*

E. A. GULBRANSEN—Has the author studied the structure of the evaporated aluminum deposit using the electron diffraction or electron microscope techniques? Has he observed the formation of a film of aluminum oxide on the surface of evaporated aluminum?

T. N. RHODIN—Electron micrographs were not taken of the surface. As far as aluminum oxide is concerned, I think everyone will agree it is absolutely impossible, under the baking conditions we can obtain in the laboratory, to get an absolutely oxide-free surface. There is enough oxygen on the surfaces of this area to produce an oxide film. The distribution of oxide in the aluminum film remains undefined. One might expect oxide particles in the metal film would promote disorder.

## Kinetics of the Reactions of Zirconium with $O_2$ , $N_2$ , and $H_2$

by E. A. Gulbransen and K. F. Andrew

DISCUSSION, M. B. Bever presiding

J. T. WABER—In the study of the oxidation reaction a parabolic rate law was observed. Such a rate law is to be expected if the reaction is under diffusion control.

Wagner and coworkers have pointed out the importance of ionic diffusion in the conduction of electricity through semiconductors such as halides and oxides, and subsequently proposed a theory for corrosion reactions. Experimentally it was observed that the ionic conductivity is proportional to the  $n$ -th power of the oxygen pressure for cationically conducting oxides, where  $n$  is a fraction ranging from one seventh to one fourth. Seitz recently showed by a radioactive tracer method, that the diffusivity calculated from the conductivity by the usual Einstein relation agrees very well with that directly measured. By this reasoning one might expect that oxidation rate might be proportional to some such  $n$ -th power of the oxygen pressure.

Indeed an analysis of the data presented in table III gave an oxygen dependence ranging from 0.3 to 0.04 for  $n$  and slowly decreasing with scale thickness. This dependence on scale thickness obscures the argument presented above and hence the revision of the  $\Delta S^\ddagger$  value, that would be necessary if the diffusivity  $D$ , were pressure dependent, can probably be neglected.

The effect of nitrogen pressure on the rate of reaction of this gas with zirconium is appreciable during the first half hour at 750°C but becomes obscure as the scale thickness increases. Therefore calculation of the pressure dependence of the parabolic rate constant from data in fig. 11 is inappropriate although investigation of this detail might be meritorious.



E. J. CHAPIN—Was there an assumption made that oxygen was not soluble in the metal at the temperature of 425°C?

J. T. WABER, *Los Alamos Scientific Laboratory, Los Alamos, N. M.*; E. J. CHAPIN, *Naval Research Laboratory, Washington, D. C.*; J. T. NORTON, *Massachusetts Institute of Technology, Cambridge, Mass.*; A. U. SEYBOLT, *General Electric Co., Schenectady, N. Y.*; M. B. BEVER, *Department of Metallurgy, Massachusetts Institute of Technology, Cambridge, Mass.*

E. A. GULBRANSEN (authors' reply)—That assumption is implied in calculating the thickness of the oxide film. The rate data are good in spite of that assumption, as you may interpret it as grams per centimeter squared. We feel that the oxide, up to 425°, is not appreciably soluble, so that the calculations in terms of thickness are fairly good. We do not know how soluble the oxide is, however, we do see these oxide films on the metal after heating for a long time in vacuum at this temperature.

J. T. NORTON—Is the oxide formed at the low temperatures on zirconium  $ZrO_2$  or  $ZrO$ ? Are there any determinations to be made?

E. A. GULBRANSEN—Dr. Hickman and I have studied this problem and find the oxide to be monoclinic  $ZrO_2$  over a wide temperature range.

A. U. SEYBOLT—What reaction occurs with CO or  $CO_2$  on zirconium?

E. A. GULBRANSEN—This problem has been studied by Guldner and Wooten. They find that both the oxide and carbide are formed. This is in accord with the predictions of thermodynamics.

M. B. BEVER—The diffusion of atomic hydrogen into zirconium is consistent with the pressure dependence of the solubility of diatomic gases in metals known as Sievert's law.

E. A. GULBRANSEN—Yes.

## Kinetics of the Reactions of Titanium with $O_2$ , $N_2$ , and $H_2$

by E. A. Gulbransen and K. F. Andrew

DISCUSSION, M. B. Bever presiding

W. J. MOORE—The authors state that the self-diffusion coefficient of titanium in its oxide is given by  $D = K/2$ , where  $K$  is the parabolic rate constant. This appears to be an over-simplification. The theoretical equation given by N. F. Mott for the rate constant is  $K = 2D(f_1 - f_2)$ , where  $f_1$  and  $f_2$  are the fractions of structural defects at the phase boundaries (interstitial ions or vacancies depending on the diffusion mechanism). In general, we do not have any quantitative information about  $f_1$  and  $f_2$ , but they usually range from  $10^{-5}$  to  $10^{-2}$ . Thus diffusion coefficients estimated from the relation  $D = K/2$  may be too low by factors of  $10^2$  to  $10^5$ .

In addition, the Mott equation itself is not firmly established. It is based on the assumption of a constant equilibrium concentration of defects at the boundaries of the oxide film. Other types of boundary conditions still lead to a parabolic rate law.

It should also be realized that "diffusion coefficients" estimated from oxidation rate constants would be valid only for the particular nonequilibrium film of oxide being formed in the oxidation. The coefficients in bulk oxide may be considerably different. In our laboratory we have studied the diffusion of radioactive copper in bulk cuprous oxide and in the oxide formed during copper oxidation. At 1000°C preliminary measurements indicate that the diffusion coefficient in the bulk oxide is smaller by a factor of about 20.

E. A. GULBRANSEN (authors' reply)—We have assumed for metals like titanium and zirconium that  $D = K/2$ . This is a simplification but it is not too bad for those oxides which have broad limits of homogeneity. Thus one may obtain approximate values for

the diffusion coefficients within a factor of  $10^{-1}$  to  $10^{-2}$  of the correct value for these oxides.

E. J. CHAPIN—What was the original oxygen content in the materials used for samples?

K. F. ANDREW (authors' reply)—We do not have an oxygen analysis on either the commercial or iodide types of titanium. Such analyses are difficult to make with a high degree of accuracy.

M. B. BEVER—Kelley's Bulletin on the thermodynamic properties of nitrides contains an equation for the decomposition pressures of titanium nitride.

E. A. GULBRANSEN—That is quite correct. There is an equation, and the decomposition pressures can be calculated. However, there is some question about certain of the present thermal data, so in our own calculations we have limited ourselves to 800°C.

H. HIRSCH—The solubility of hydrogen in titanium vs. temperature curves indicates that the solubility increases with increasing temperature. In many hydrogen-metal systems, generally the total solubility increases as the temperature is lowered. Were any samples heated to a high temperature, saturated with hydrogen, and then held at lower temperatures to determine the maximum solubility vs. temperature? Such a procedure often avoids interference from obstructing surface films.

W. J. MOORE, *Catholic University, Washington, D. C.*; E. J. CHAPIN, *Naval Research Laboratory, Washington, D. C.*; M. B. BEVER, *Department of Metallurgy, Massachusetts Institute of Technology, Cambridge, Mass.*; H. HIRSCH, *General Electric Co., Schenectady, N. Y.*; J. T. WABER, *Los Alamos Scientific Laboratory, Los Alamos, N. M.*; W. A. ALEXANDER, *National Research Council, Ottawa, Ont., Canada.*

E. A. GULBRANSEN—We have not made solubility experiments of hydrogen in titanium. This has been done by others. Our interest is chiefly in the rate of reaction. Here the effect of temperature is to increase the rate at which hydrogen is taken up by the metal.

J. T. WABER—I would like to point out a minor improvement that the authors might make. Their rate expression is

$$K = \frac{2KT}{h} \lambda^2 \exp \left( \frac{\Delta S^*}{R} - \frac{\Delta E^*}{RT} \right) \quad [1]$$

which can be written in the logarithmic form

$$\ln K = \ln A + \ln T - \left( \frac{\Delta E^*}{R} \right) \frac{1}{T} \quad [2]$$

wherein  $A$  has been appropriately defined to include the constant terms of eq 1. The authors have plotted the function  $\ln K$  against  $(1/T)$  to obtain the energy of activation  $\Delta E^*$  from the slope. It is apparent that this procedure is equivalent to neglecting the second term on the right hand side of eq 2. A preferable procedure would be to plot the function  $\ln (K/T)$  against the reciprocal of the absolute temperature.

In recent experiments on the oxidation of "iodide" titanium by air, a considerable weight loss occurred that is unaccounted for. During the period of the weight loss, appreciable thicknesses of an oxide film developed, as was indicated by the interference colors. A summary of pertinent data follows.

Sample No.	Temp, °C	Elapsed Time, Hr	Total Wt. Loss, Micrograms
1	220	40.5	1,049
2	250	43.5	674
3	320	43.5	730
1A	220	540.	1,331
2A	250	1451.	159
3A	320	1451.	56
1AA	320	898	252 (Gain)



The repeated runs 1A, 2A and 3A were polished dry to eliminate the possibility that the weight loss was due to adsorbed moisture. Even in a short time, the oxide thickness was appreciable. In run No. 3, the oxide was 390 Å thick at the end of 43 hr. Further investigation has revealed that this weight loss behavior can be prevented by adequate vacuum treatment, but the constituent has not been identified.

In a discussion of TP 2659 by the same authors I pointed out that a pressure dependence of reaction rate might be expected to lie in the range of the one fourth power of the oxygen pressure. Such a prediction was based on the semitheoretical ideas of Wagner concerning semiconductors such as oxides and halides. Analysis of the data in fig. 4 leads to the rate expression

$$K = kp^n$$

wherein  $n = 0.33$  for scale thicknesses corresponding to the conclusion of the experiment, and this exponent seems to hold over the complete range of thickness investigated.

A small revision of the entropy of activation is necessary as the theory of absolute reaction rates is based on specific rate constants such as  $k$  rather than  $K$ . The choice of 1 atm of pressure appears to be a satisfactory standard state to simplify the dimensions of the constant  $k$ . Thus  $P$  can represent the reduced pressure of the absolute partial pressure  $p$  divided by 1 atm. The comparison of the entropy of activation with those calculated by construction of a model could be facilitated by expressing  $k$  in the units of mols reaction per square centimeter per second instead of the units herein employed.

E. A. GULBRANSEN—Dr. Waber's point about plotting  $\ln K/T$  instead of  $\ln K$  is well taken, and will be employed in the future. For most cases the change in the temperature  $T$  is small compared to changes in  $\ln K$ . A similar energy of activation would be calculated from either plot.

We have heated one of Dr. Waber's samples in high vacuum over a wide temperature range and find no unusual behavior. The weight loss observed in Dr. Waber's measurements must be attributed to material evolved on evacuating and heating to 300°C.

We do not feel that the vacuum microbalance is the most desirable instrument for measuring pressure effects on reaction rates since convection currents are present in the system due to temperature differences. Unless great care is exerted it is difficult to separate gas flow effects due to convection currents and their pressure dependency from the pressure effect. This we have not done.

We prefer to express our data in terms of diffusion theory since this gives us a chance to compare with diffusion data from other types of systems.

W. A. ALEXANDER—What was the nature and quantity of the gas pumped out in the early part of the experiments?

K. F. ANDREW—The gas given off is rather small and thus it is difficult to analyze even by mass spectrometer techniques. We have no evidence of the composition of these gases.

## The Lattice Parameters of High Purity Alpha Titanium; and the Effects of Oxygen and Nitrogen on Them

by H. T. Clark, Jr.

DISCUSSION, B. W. Gonser presiding

E. S. GREINER—Impurities such as those present in this titanium (footnote of table III) will affect the size of the unit cell. Iron, silicon, and aluminum probably enter the close-packed hexagonal lattice of titanium in a substitutional manner because of similarity in the atomic radii. Since the radius of each of these metallic

impurity atoms is smaller than that of titanium, the size of the unit cell should be decreased by their presence. I wish to ask the author if he has any information concerning whether this reduction in size of the unit cell will affect the values of  $a_0$  and  $c_0$ , or only that of  $c_0$ , as was found for the impurities, oxygen and nitrogen, which are probably interstitial.

B. W. GONSER—The value of  $c_0$  referred to in the second footnote of table I was from a single determination, incidental to work on properties other than lattice parameters. Filings of iodide titanium (made under the same conditions as were used in making the titanium for Mr. Clark) were sealed in a hole drilled in a section of iodide titanium rod and vacuum annealed before X-ray examination. The powder easily could have become contaminated in processing, and we readily agree that the use of sheet specimens would be better. Mr. Clark's method of preparation probably could have been improved also, by merely cold rolling the iodide titanium rod as received, and vacuum annealing, in place of melting, rolling, annealing, surface grinding, and annealing again. Every operation adds to the risk of contamination.

E. S. GREINER, Bell Telephone Laboratories, New York, N. Y.; B. W. GONSER, Battelle Memorial Institute, Columbus, Ohio.

H. T. CLARK (author's reply)—Determinations of the parameters of titanium-aluminum alloys have shown that both the  $a_0$  and  $c_0$  values of the alpha phase are decreased by the addition of aluminum. No determinations have been made on systems containing the other two elements about which Dr. Greiner asked.

Two X-ray samples have been prepared directly from the iodide rod by cold rolling as suggested by Dr. Gonser. The parameters of these samples were not significantly different from those reported in table III.

## The Effect of Oxygen, Nitrogen, and Hydrogen on Iodide Refined Titanium

by R. I. Jaffee and I. E. Campbell

DISCUSSION, B. W. Gonser presiding

E. A. GULBRANSEN—Should the hardness data be represented as single points or would it be better to give the range of values observed?

R. I. JAFFEE (authors' reply)—Dr. Gulbransen raises a very good point. It certainly is true for large grained alpha titanium. In large grained titanium there are orientation effects from the various grains insofar as hardness is concerned. The alloys are somewhat different. Orientation effects are generally greatest in the as-deposited iodide titanium. The specimens in this work had received about 90 pct cold-reduction before being annealed and recrystallized. Therefore, orientation effects should be minimized. I would say that, in this case, average hardness is satisfactory.

E. A. GULBRANSEN, Westinghouse Research Laboratories, East Pittsburgh, Pa.; A. U. SEYBOLT, General Electric Co., Schenectady, N. Y.

A. U. SEYBOLT—In connection with the remarks on the Widmanstätten structure, it might be pointed out that some recent Russian work has shown that there is a martensite transformation possible in cooling from beta to alpha zirconium. The type of structure shown in the micrographs might suggest such a transformation mechanism in the specimens used by Jaffee.

Also, the fine grained Widmanstätten structure shown in the zirconium-nitrogen alloys might be due to the effect of nitrogen on the kinetics of the beta → alpha transformation. Nitrogen might lower the transformation temperature enough so that nucleation of alpha occurs at a lower temperature than in the pure metal. Since more alpha nuclei would be present when formed at a low temperature, a fine grained structure would be expected.



R. I. JAFFEE—There undoubtedly is martensitic transformation when titanium is quenched fast enough. The rate of cooling in this case was slow enough that a true Widmanstätten arrangement of plates was obtained. In connection with Dr. Seybolt's remarks on the cause for the finer plates in the nitrogen-containing alloys, I agree, completely, with him.

## Preparation and Casting of Beryllium Melts

by J. G. Kura, J. H. Jackson, M. C. Udy,  
and L. W. Eastwood

DISCUSSION, H. Y. Hunsicker *presiding*

E. J. BOYLE—Were any analyses made of impurity content, especially carbon?

L. W. EASTWOOD (authors' reply)—As reported in the paper, the impurities found in remelted virgin beryllium were 0.10 pct Al, 0.08 pct Si, 0.10 pct Fe, < 0.05 pct Mg, and only traces of other elements. Metallographic examination revealed just a few carbides which indicated the metal had relatively low carbon content. The actual carbon content may be as high as 0.05 pct. Analytical methods for carbon were not so precise as desired. Presence of carbide has been found in samples reported to contain 0.005 pct carbon.

S. J. MORANA—To your knowledge, is there any evidence of diffusion of oxygen and/or nitrogen in metallic beryllium? I refer to a true diffusion similar to that reported in experiments conducted with metallic titanium.

L. W. EASTWOOD—We gave a lot of thought to this problem, because it does have a very real bearing on the problem of unsoundness in the beryllium castings. Particularly, gas solubility in the liquid is important. We were unable to show any evidence of solubility of oxygen in beryllium. However, there may be some solubility of oxygen in the liquid or solid beryllium. We did not have any evidence of solubility of nitrogen in solid beryllium, but we do have distinct evidence that nitrogen is soluble in beryllium melts.

A. HILLER—What were the maximum densities obtained for fairly sound castings? What safety precautions were taken in handling beryllium or in disposing of the argon atmospheres?

E. J. BOYLE, Oak Ridge National Laboratory, Oak Ridge, Tenn.; S. J. MORANA, Clifton Products, Inc., Painesville, Ohio.; A. HILLER, General Electric X-Ray Corp., Milwaukee, Wisc.

L. W. EASTWOOD—We did not measure any densities of the beryllium. One would have to be reasonably careful in measuring the density of beryllium, because it would be enormously affected by the composition. Because of the low density of the beryllium, any heavy metallic impurities will have a very substantial effect on density. The unsoundness that we encountered was entirely that of shrinkage if it was inadequately fed, or fairly large gas or blowholes if the gas was excessively high in the melt. Both are readily visible and density measurements do not appear necessary.

I would suspect that difficulties with leakage in beryllium would be a result of poor feeding.

Careful attention should be paid to the attainment of proper temperature gradients in the casting at the time it is poured.

The hazard involved in handling beryllium is, of course, a fairly complex question, entirely out of my field. I would say that anyone who is handling beryllium, or contemplates handling beryllium, should be thoroughly familiar with this problem. There is a lot of information on it, and I believe it is obtainable through the A.E.C.

## Metallographic Examination of Beryllium Alloys

by M. C. Udy, G. K. Manning, and L. W. Eastwood

DISCUSSION, H. Y. Hunsicker *presiding*

H. S. KALISH—We found that all phases in the beryllium-zirconium system could be identified using polarized light almost exclusively. Alloys with 5 or 10 pct Zr, lightly etched with 5 pct HF, were similar to that shown in fig. 22 and could be seen equally well unetched with polarized light. When properly polished, the beryllium matrix grains are clearly visible in polarized light, and the more arduous preparation described by the authors can be avoided.

W. A. ALEXANDER—In studying the recrystallization of beryllium, we found and reported previously that new grains, invisible in ordinary light, were shown more clearly in polarized light.

H. S. KALISH, Sylvania Electric Products Inc., Bay-side, L. I., N. Y.; W. A. ALEXANDER, National Research Council, Ottawa, Ont., Canada.

M. C. UDY (authors' reply)—Of course, we recognized the usefulness of polarized light in examining beryllium specimens. This has been used for quite a long time. The M.I.T. work described this method quite fully. However, since the "arduous" preparation described by the authors consisted of obtaining a proper polish, it is hard to see how use of polarized light could avoid anything but our simple etching procedure. I am happy to hear from Mr. Kalish that the 5 pct zirconium alloy of ours looked much the same as did his.

## Kinetics of the Austenite → Martensite Transformation

by J. C. Fisher, J. H. Hollomon, and D. Turnbull

DISCUSSION, A. E. Nehrenberg *presiding*

L. D. JAFFE—The authors assume that the nuclei or embryos from which the martensite needles grow are not coherent with the parent austenite lattice, otherwise the embryos would not persist long enough to nucleate the martensite at the proper temperature. They assume, on the other hand, that the martensite is coherent with the austenite after it is grown. This divergency is explained on the basis that the advancing martensite front leaves behind it dislocations which were originally at the martensite-austenite interface. It would seem equally reasonable for the austenite to advance into the embryos, leaving behind dislocations, and at the same rate. That rate is very fast and the embryos would not remain in their high temperature distribution during quenching, so that they would not be available to nucleate the martensite at the proper temperature.

L. D. JAFFE, Watertown Arsenal Laboratory, Watertown, Mass.

J. C. FISHER (authors' reply)—The question raised related to the exact sort of embryo that was assumed to be retained during quenching from the austenitizing temperature. There are a number of possibilities. The one mentioned in the paper was that a little particle of noncoherent ferrite in a carbon-free region could be retained during quenching. This, however, is not a necessary picture, and we now feel that another possibility is more likely, although I do not believe it was so stated in the paper. Certainly if there are carbon-free regions in the austenite, these regions will persist during quenching because it takes the carbon a relatively long time to move by diffusion. Little coherent martensite plates will form and disappear by thermal motion in such carbon-free regions during



quenching, until finally during cooling a little plate forms that can persist (the critical size decreases at lower temperatures) in carbon-free austenite—in other words, in pure gamma iron—so that it remains in the carbon-free region until the  $M_s$  temperature is reached and the platelet can grow out and fill the specimen.

We now feel that it is more likely that the martensite nucleus arises in this way, by little martensite platelets flicking in and out during quenching until the temperature gets low enough so the last platelet formed will persist on down to the  $M_s$  temperature or below. The arguments that led us to come to this conclusion were substantially the arguments that Dr. Jaffe has just presented.

## The Free Energy Change Accompanying the Martensite Transformation in Steels

by J. C. Fisher

DISCUSSION, G. M. Cover presiding

P. K. KOH—In these calculations, is the variation in the pressure resulting from the volumetric change during the martensitic transformation considered?

B. L. AVERBACH—The author has presented a thermodynamic treatment of the martensite transformation if it is considered as a process of nucleation and growth. Cohen and Paranjpe have presented another thermodynamic treatment of the same transformation considered as a process of nucleation and shear. A main point of difference in these two views comes in deciding whether tetragonal martensite or cubic martensite is the thermodynamically stable structure. The author assumes that the tetragonal form is the stable one, whereas the other authors have decided in favor of the cubic form. This point would best be answered experimentally and it is hoped that some experiment can be devised to test these hypotheses.

P. K. KOH, *Allegheny Ludlum Steel Corp., Breckensridge, Pa.*; B. L. AVERBACH, *Massachusetts Institute of Technology, Cambridge, Mass.*

J. C. FISHER (author's reply)—First of all, to reply to Dr. Koh, the pressure was completely ignored in the analysis. The fact that martensite particles are plates, and can pry the austenite apart fairly easily, suggests that the influence of pressure would be considerably less than if the particles formed as spheres.

In reply to Dr. Averbach, I think there is evidence that the tetragonal form of martensite, when it is observed, is more stable than the cubic, and the evidence, briefly, is this. When one looks at martensite it is tetragonal, and it remains so at temperatures where we know that carbon moves around rapidly. At room temperature, for example, carbon stays in any given interstitial position only about 1 sec.

One would think if the cubic form were the more stable, transformation to cubic martensite would occur in a matter of seconds. The fact that it stays tetragonal for relatively long times suggests strongly, I think, that the tetragonal form is the more stable one.

## The Transformations in $\beta$ -CuAl Alloys

by E. P. Klier and S. M. Grymko

DISCUSSION, J. C. Fisher presiding

D. J. MACK—It is to be expected that as one departs from the eutectoid composition in either direction there will be some changes in the decomposition of the  $\beta$ , but the changes which occur may be less complex than indicated in this paper. Since this system shows a ready tendency to form metastable or transition phases, particularly supersaturated phases, it is logical to expect the greatest departure from customary eutectoid behavior in the hyper-eutectoid direction. The rightward shift in the diagram with increased cooling rate

proposed by Smith and Lindlieff<sup>2</sup> to account for the precipitation of supersaturated  $\alpha$  indicated that alloys up to about 12.8 pct Al should transform similarly to the eutectoid alloy. Koch<sup>3</sup> and Gridnew<sup>4</sup> agreed on the value of 12.8 pct Al. Fig. 33 shows the structure of a high purity alloy containing 12.47 pct Al transformed 20 hr at 400°C. The structure, consisting of pre-eutectoid Widmanstätten  $\alpha$  and pearlite, is essentially the same as that of a eutectoid alloy transformed at the same temperature-time. Fig. 34 shows a hyper-eutectoid alloy containing 12.75 pct Al which was also transformed 20 hr at 400°C. The structure consists of pre-eutectoid  $\gamma_2$  and pearlite in the untransformed matrix. This alloy, although containing only 0.30 pct Al more than that shown in fig. 33, is clearly hyper-eutectoid and has what might be termed a "normal" hyper-eutectoid structure. This means that the metastable eutectoid composition postulated by Smith and Lindlieff, Koch, and Gridnew actually lies between 12.47 and 12.77 pct Al—in good agreement with their value of 12.8 pct Al.

The authors have shown that the character of the decomposition of  $\beta$  undergoes a marked change when the aluminum content is further increased to 13.5 pct—departing radically from normally expected hyper-eutectoid behavior. One is reluctant to give up the idea of structural analogy in similar alloy systems. Figs. 35, 36, and 37 indicate that this structural analogy may still be valid in the copper-aluminum system. The alloys shown in these three micrographs were all transformed isothermally 20 hr at 400°C. Fig. 35 shows pearlite in an alloy of 9.22 pct Al, fig. 36 in an alloy of 10.66 pct Al.

It is true that the pearlite in figs. 35 and 36 is not uniformly lamellar but this is apparently because the spacing of the martensite  $\beta'$  needles is of the same order of magnitude as the spacing of the pearlite which would normally form at this temperature. Consequently, the  $\beta'$  interferes with the development of uniform lamellar pearlite. There are many times when the pearlite in steel is not uniform<sup>5</sup> and yet we do not hesitate to call it pearlite. Actually, it is rather amazing that pearlite appears in these aluminum bronzes at all when one considers the complex parent phases from which it forms. Fig. 37 shows lamellar pearlite in an alloy of 15.16 pct Al. The  $\beta$  in this alloy seems to decompose in a manner similar to that described by the authors for their 13.5 pct Al alloy, but ultimately ends up as pearlite. It seems the situation for this hyper-eutectoid alloy is analogous to the isothermal decomposition of  $\beta$  in the hypo-eutectoid alloys below the nose of the T-T-T curve. In both cases the  $\beta$  transforms to an intermediate structure which in turn transforms to pearlite. These intermediate structures are different in the hypo and hyper-eutectoid alloys.

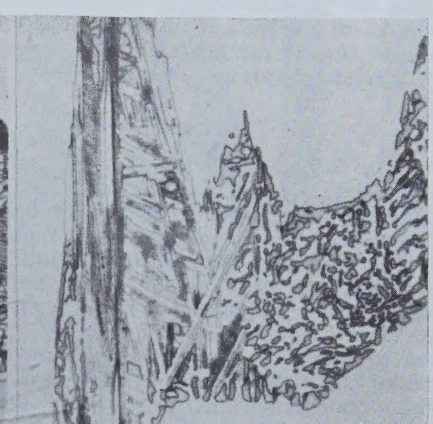
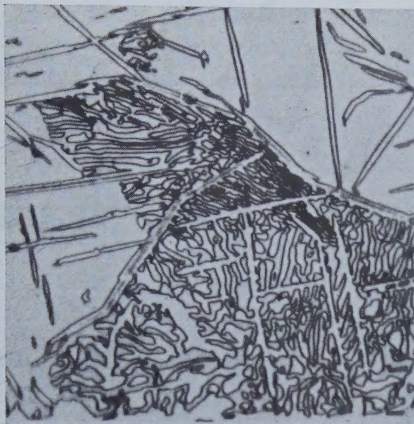
Since the structures shown in figs. 34 and 37 have extensive pre-eutectoid  $\gamma_2$  one wonders why it appears in these alloys but not the 13.5 pct Al alloy. It seems illogical that differences in "austenitizing" temperature, atmosphere, salt bath or prior thermal and mechanical treatment could account for the observed difference. We know that iron in aluminum bronzes alters the appearance of the transformation products and perhaps even the mechanism of transformation. Do the authors have information on the iron content of their alloys? Such data may reconcile the differences.

D. J. MACK, *Department of Metallurgical Engineering, University of Wisconsin, Madison, Wisc.*

E. P. KLIER (authors' reply)—We are hesitant to attach significance to the concept of "metastable eutectoid composition" which Dr. Mack associates with transformation phenomena in this system, largely because it finds no analogue in the more thoroughly studied iron-carbon system, where the "metastable eutectoid composition" shifts in the direction of both high and low carbon contents.

In discussing the structures which Dr. Mack presents in support of the concept of "metastable eutectoid





36

37

**Figs. 33-37 — Aluminum bronze containing varying amounts of Al, Fe, Ni, and Mn.**

X1000. All specimens etched electrolytically in 1 pct chromic acid. Isothermally transformed 20 hr at 400°C.

Fig. 33—12.47 pct Al 0.03 pct Ni, and trace Fe. Supersaturated Widmanstätten  $\alpha$  and pearlite.

Fig. 34—12.75 pct Al, 0.21 pct Fe. Pre-eutectoid  $\gamma_2$  along old  $\beta$  grain boundary (bottom of picture) and pearlite.

Fig. 35—9.22 pct Al, 0.15 pct Fe, and 0.02 pct Mn. Massive pre-eutectoid  $\alpha$ , tempered  $\beta'$  partially transformed to pearlite.

Fig. 36—10.66 pct Al, 0.17 pct Fe, and 0.02 pct Ni. Tempered  $\beta'$  and pearlite.

Fig. 37—15.16 pct Al, 0.07 pct Fe. Massive pre-eutectoid  $\gamma_2$ , and the transition structure partially transformed to pearlite.

composition," it is pointed out that an inconsistency with our data has not been certainly shown to exist. We have treated no specimens which could be compared to those discussed by Dr. Mack, nor has he reported results which can be properly compared to the data which we have reported. The temperature interval 425° to 375°C which we did not cover may be particularly revealing.

Finally, it is pointed out that our work leans heavily on the X-ray data reported, and structures have been identified and correlated, insofar as possible, by means of these X-ray data. This leads to a deviation from Dr. Mack's identification of microstructures. The X-ray data, however, while offering no conflict with the metallographic results, have allowed the determination of the crystal structures involved in the course of decomposition of the  $\beta$  phase, and therefrom the discussion of a possible mechanism whereby this decomposition is achieved. These data have already been fully discussed.

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- <sup>5</sup> R. A. Grange: Factors Influencing the Pearlitic Microstructure of Annealed Hypo-Eutectoid Steel. *Trans. ASM* (1947) 38, 879.

### Transformation of Gamma to Alpha Manganese

by E. V. Potter, H. C. Lukens, and R. W. Huber

DISCUSSION, G. Edmunds presiding

R. O. WILLIAMS—The authors are to be congratulated on carrying out an excellent program of research on a fundamental problem of such wide interest. It

would seem that their method of following the reaction was simple, accurate experimentally, and, in general, very satisfactory. It is, however, doubtful that their first equation,

$$R = \alpha R_\alpha + \gamma R_\gamma \quad [12]$$

is accurate.

A more general equation has been derived giving the following form:

$$R = \frac{R_\gamma + y(R_\alpha - R_\gamma)}{\left(\frac{R_\alpha - 1}{R_\gamma}\right)(y - \alpha) + 1} \quad [13]$$

All the terms have the same meaning as in the paper. The new term,  $y$ , is what might be called a geometric factor considering the possible geometric arrangements for two phases and having a possible range of values from  $\alpha$  to 1. It will be found that for  $y = \alpha$  the equation simplifies to

$$R = \alpha R_\alpha + (1 - \alpha) R \quad [14]$$

which is the same as eq 13 since it is assumed that

$$\gamma = 1 - \alpha \quad [15]$$

This equation can be interpreted by thinking of the direction of current being perpendicular to a series of plates of the two different phases. It will be found that this gives the highest possible value for the resistivity of a solid two-phase mixture.

When  $y$  has its maximum value, 1, the equation reduces to the following form:

$$R = \frac{R_\alpha R_\gamma}{(1 - \alpha) R_\alpha - \alpha R_\gamma} \quad [16]$$

This form can be viewed as the resistance measured by having the current flow parallel to a series of plates of the different phases. It will be found that this gives a minimum value for resistivity for any composition.

Eq 13 does not consider the possible effect of grain size, internal stresses, or possible discontinuities in the



metal. The equation is not implicit since it gives no value for  $y$ . However, a value of  $y$  suggested in the method of derivation is  $\alpha^{1/3}$ . There is no reason to believe that a more accurate expression for  $y$  could be expressed as simply as

$$y = \alpha^x, \quad 0 \leq X \leq 1 \quad [17]$$

From a casual observation of the problem, it is believed that the most important influence on the possible values of  $y$  would be the geometry of the two phases. This would include what might be called preferred orientation as regards to both crystallographic directions and grain shape. Grain size might be very important as evidenced by the increase in the resistivity of metal being cold-worked. The easiest solution to this dilemma would then seem to be experimental work if possible. A more exacting calculation might be made, but this would seem to require knowledge not generally known, as well as difficult calculations as involved in similar problems. Even this would need some experimental backing.

Table XIV has been included to show the magnitude of differences between the values as obtained by eqs 12 and 13 using a value of  $y = \alpha^{1/3}$  for the data obtained at 140°C. Plotting  $\log \alpha/\gamma$ , as determined by the modified equation, revealed that there was greater deviation from a straight line than before. The foot of the curve was flatter and longer than before, and the top of the curve bent down somewhat. While the value of  $\log \alpha/\gamma$  was greater at the start, its rate of increase was less, hence the flatter the toe to the curve. No modification of the rate equation was attempted. However, the graph of  $\log \alpha/\gamma$  resembled that expected from a phase transformation where the rate of nucleation is proportional to the untransformed volume; and the rate of transformation is proportional to the surface area between the two phases.

**Table XIV. Comparison of Values of Transformed Volume Based Upon Eqs 12 and 13 for 140°C**

$R^*$	$\alpha$ Eq 12	$\alpha^\dagger$ Eq 13	$\Delta \alpha$
73.1	0.00	0.00	0.00
84.4	0.10	0.16	0.06
96.0	0.20	0.312	0.112
97.4	0.30	0.444	0.144
118.8	0.40	0.560	0.160
132.7	0.50	0.680	0.180
142.0	0.60	0.751	0.151
153.4	0.70	0.826	0.126
164.8	0.80	0.890	0.09
176.2	0.90	0.950	0.05
187.6	1.00	1.00	0.00

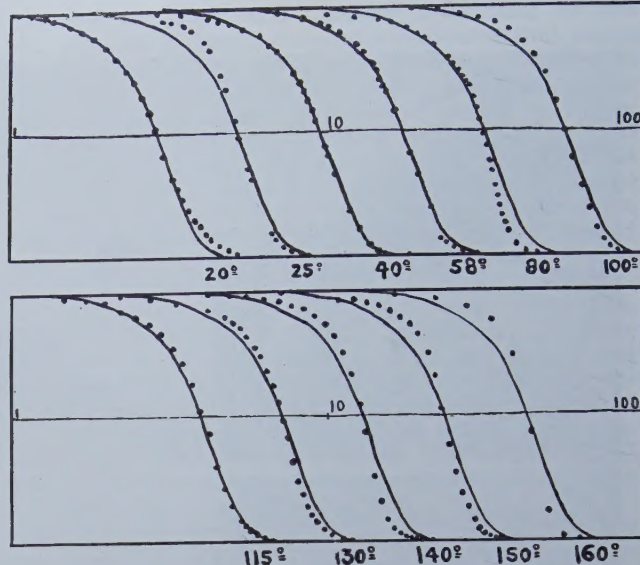
\* Note that the values for  $R_\alpha$  and  $R_\gamma$  were taken as the values best fitting the equations as presented in the paper.

† Values based on  $y = \alpha^{1/3}$ .

J. T. WABER—A plot of the logarithm of the reaction rate constant  $K$  against the reciprocal of absolute temperature does not permit the calculation of the free energy of activation,  $\Delta F^\ddagger$ . The slope of this line is the energy  $\Delta E^\ddagger$  or  $\Delta H^\ddagger$  since the  $\Delta S^\ddagger$  occurs in the temperature independent terms of eq 11. The authors are to be complimented on the use of the accurate expression  $\log (K/T)$  rather than  $\log K$  for the ordinate although the latter is more common because  $\log T$  varies very slowly in comparison with the other terms. Therefore  $\Delta E^\ddagger$  is 21.1 kcal.

In closing, I wonder if the authors have considered the possibility of a mechanism involving consecutive reactions, such as  $\gamma \rightarrow x \rightarrow \alpha$ , wherein  $x$  is a transient phase. The percentage transformation curve, fig. 1,

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**Fig. 6—Fraction of alpha transformed plotted as a function of the log time.**

looks like those which are observed for such a chain of reactions.

P. LAURENT and M. BATISSE—The allotropic transformation data may also be interpreted by the theory of Johnson and Mehl.<sup>8</sup> If the fraction of alpha transformed is plotted as a function of the log time, a

<sup>8</sup> W. A. Johnson and R. F. Mehl: Reaction Kinetics in Processes of Nucleation and Growth. *Trans. AIME* (1939) 135, 416.

series of superimposable curves is obtained transposed along the log-time axis. These are shown as the experimental points in fig. 6 together with the curves of Johnson and Mehl fitted at the half-transformation points. (For the convenience of plotting, the points from table XIII have been reduced by an equal arbitrary amount which does not change the shape of the plots.) In general the points fit the curves particularly at 40°, 58°, and 115°. The deviations at the four highest temperatures may be because the time of heating the specimens to the transformation temperature may not be negligible compared to the transformation time. The deviations at 20° and 25° may be the result of heating the specimens to 30° during electrolytic deposition. Other deviations may be because the rates of nucleation and growth are not constant during the transformation. It is believed that the manganese had a preferred orientation as a result of electrolytic deposition so that anisotropic growth caused deviations from the theory. Can the authors describe the texture of their electrodeposited manganese?

R. W. HUBER (authors' reply)—Mr. Williams' relation, eq 13 for the resistance of a two phase alloy is very interesting. It could well be a more accurate representation of the resistance than the authors' relation if the factor  $y$  can be determined accurately. The authors' relation is obviously too simple but it can be handled mathematically quite readily and represents the data surprisingly well.

The possibility of an intermediate phase occurring in the transformation from gamma to alpha manganese was considered. It might be expected that beta manganese would be present at some time but no evidence of this phase was ever found.

The interest shown by Messrs. Laurent and Batisse in this work is very gratifying. It was the authors' hope in presenting this data that others might be interested in interpreting it. The material used in these tests is described in a paper by Schlain and Prater.<sup>9</sup> It is suggested that information relative to the preparation and structure of the manganese sheets used in these tests be obtained from this source where a complete description is available.